Section IV

ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

5 Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of CH_1 , CH_2 , and C-C. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes 10 section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, 15 urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by 20 using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at 25 http://www.blacklightpower.com/bookdownload.shtml which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant k' of a

H₂-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where C_1 is the fraction of the H_2 -type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of H bonding to a 5 central atom and 0.5 (Eq. (14.152)) otherwise, and C_2 is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.2)

10 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO b = c is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_{e} = n_{1}c_{1}c_{2}\frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2}-b^{2}}}\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(15.6)

The potential energy of the two nuclei is

$$V_{p} = n_{1} \frac{e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}}$$
 (15.7)

The kinetic energy of the electrons is

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$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(15.8)

And, the energy, V_m , of the magnetic force between the electrons is

$$V_{m} = n_{1}c_{1}c_{2}\frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}}\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(15.9)

The total energy of the H_2 -type prolate spheroidal MO, $E_T(H_1MO)$, is given by the sum of the energy terms:

$$E_T(\mu_2 MO) = V_e + T + V_m + V_D \tag{15.10}$$

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$
(15.11)

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where n_1 is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by c_{BO} , the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules, and 9 for an 10 independent triplet bond. Then, the kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. c_1 is the fraction of the H_2 -type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of H bonding to an unhybridized central atom and 1 otherwise, and c_2 is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals 15 of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the H_2 -type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor c_2 of a H_2 -type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H, (iii) the ratio of 20 the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two c_2 factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different c_2 factors corresponding to any of the cases (i)-(v). Specific examples of the factor c_2 of a H_2 -type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.91771, the ratio of 14.82575
$$eV$$
, $-E_{Coulomb}(C,2sp^3)$, and 13.605804 eV ; 0.87495, the ratio of 15.55033 eV , $-E_{Coulomb}(C_{ethane},2sp^3)$, and 13.605804 eV ; 0.85252, the ratio of 15.95955 eV , $-E_{Coulomb}(C_{ethylene},2sp^3)$, and 13.605804 eV ; 0.85252, the ratio of 15.95955 eV , $-E_{Coulomb}(C_{ethylene},2sp^3)$, and 13.605804 eV , and 0.86359, the ratio of 15.55033 eV , $-E_{Coulomb}(C_{olkane},2sp^3)$, and 13.605804 eV .

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy E_T (atom, msp^3) (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell.

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$$E_T(atom, msp^3) = -\sum_{m=1}^{n} IP_m$$
 (15.12)

where IP_m is the *m*th ionization energy (positive) of the atom. The radius r_{msp^3} of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T \left(atom, msp^3\right)}$$
(15.13)

Then, the Coulombic energy $E_{Coulomb}$ (atom, msp^3) of the outer electron of the atom msp^3 20 shell is given by

$$E_{Coulomb}\left(atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.14)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron:

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$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.15)

Then, the energy $E(atom, msp^3)$ of the outer electron of the $atom msp^3$ shell is given by the sum of $E_{Coulomb}(atom, msp^3)$ and E(magnetic):

$$E(atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.16)

Consider next that the at least two atomic orbitals hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the hybridized orbitals is given by the sum of $E(atom, msp^3)$ and the next energies of successive ions of the atom over the n electrons comprising the total electrons of the at least two initial AO shells. Here, $E(atom, msp^3)$ is the sum of the first ionization energy of the atom and the hybridization energy. An example of $E(atom, msp^3)$ for $E(C, 2sp^3)$ is given in Eq. (14.503) where the sum of the negative of the first ionization energy of C, -11.27671 eV, plus the hybridization energy to form the $C2sp^3$ shell given by Eq. (14.146) is $E(C, 2sp^3) = -14.63489 eV$.

Thus, the sharing of electrons between two $atom \, msp^3$ HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each $atom \, msp^3$ 20 HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy E_T (mol.atom, msp³) (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_{T}\left(mol.atom, msp^{3}\right) = E\left(atom, msp^{3}\right) - \sum_{m=2}^{n} IP_{m}$$
(15.17)

where IP_m is the *m*th ionization energy (positive) of the atom and the sum of $-IP_1$ plus the hybridization energy is $E(atom, msp^3)$. Thus, the radius r_{msp} , of the hybridized shell is given by:

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$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25)\right) \frac{-e^2}{8\pi\varepsilon_0 E_T \left(mol.atom, msp^3\right)}$$
 (15.18)

where s = 1, 2, 3 for a single, double, and triple bond, respectively. The Coulombic energy $E_{Coulomb}$ (mol.atom, msp³) of the outer electron of the atom msp³ shell is given by

$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.19)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired 10 in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}(mol.atom, msp^3)$ and E(magnetic):

$$E(mol.atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.20)

15 E_T (atom – atom, msp^3), the energy change of each atom msp^3 shell with the formation of the atom-atom-bond MO is given by the difference between E (mol.atom, msp^3) and E (atom, msp^3):

$$E_{T}(atom-atom,msp^{3}) = E(mol.atom,msp^{3}) - E(atom,msp^{3})$$
(15.21)

As examples from prior sections, $E_{Coulomb}$ (mol.atom, msp³) is one of:

20
$$E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$$
, $E_{Coulomb}\left(C_{ethone}, 2sp^3\right)$, $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$, and $E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$;

$$E_{Coulomb}$$
 (atom, msp³) is one of $E_{Coulomb}$ (C, 2sp³) and $E_{Coulomb}$ (Cl, 3sp³);

$$E(mol.atom, msp^3) is one of E(C_{ethylene}, 2sp^3), E(C_{ethane}, 2sp^3),$$

$$E(C_{acetylene}, 2sp^3) E(C_{alkane}, 2sp^3);$$

$$E(atom, msp^3)$$
 is one of and $E(C, 2sp^3)$ and $E(Cl, 3sp^3)$;

$$E_r$$
 (atom – atom, msp^3) is one of $E(C-C,2sp^3)$, $E(C=C,2sp^3)$, and $E(C\equiv C,2sp^3)$;

5 $atom msp^3$ is one of $C2sp^3$, $Cl3sp^3$

$$E_T\left(atom-atom(s_1),msp^3\right)$$
 is $E_T\left(C-C,2sp^3\right)$ and $E_T\left(atom-atom(s_2),msp^3\right)$ is $E_T\left(C=C,2sp^3\right)$, and

$$r_{msp}$$
 is one of r_{C2sp^3} , $r_{ethane2sp^3}$, $r_{ethylene2sp^3}$, $r_{acetylene2sp^3}$, $r_{alkane2sp^3}$, and r_{Cl3sp^3} .

In the case of the C2sp3 HO, the initial parameters (Eqs. (14.142-14.146)) are

10
$$r_{2sp}^{7} = \sum_{n=2}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0} \left(e148.25751 \ eV\right)} = \frac{10e^{2}}{8\pi\varepsilon_{0} \left(e148.25751 \ eV\right)} = 0.91771a_{0}$$
 (15.22)

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \ eV \tag{15.23}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2 h^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \text{ eV}$$
 (15.24)

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{2\varphi^{3}}} + \frac{2\pi\mu_{0}e^{2}h^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(15.25)

In Eq. (15.18),

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$$\sum_{q=Z-n}^{Z-1} (Z-q) = 10$$
 (15.26)

Eqs. (14.147) and (15.17) give

$$E_T$$
 (mol.atom, msp³) = E_T (C_{ethane} , 2sp³) = -151.61569 eV (15.27)

Using Eqs. (15.18-15.28), the final values of r_{C2sp^3} , $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$, and the resulting $E_r(C^{BO}_{-C},C2sp^3)$ of the MO due to charge donation from the HO to the MO where

C-C refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1. The final values of r_{C2sp^3} , $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_r(C^{BO}_r, C^{CO}_r)$ of the MO due to charge donation from the HO to the MO where C^{BO}_r refers to the bond order of the carbon-carbon bond.

MO Bond Order (BO)	s i	s 2	$r_{C2sp^3}\left(a_0\right)$ Final	$E_{Coulomb}\left(C2sp^3\right)$ (eV) Final	$E\left(C2sp^3\right)$ (eV) Final	$E_T \left(C - C, C2sp^3 \right)$ (eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
III	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy $E(mol.atom, msp^3)$ of the outer electron of the atom msp^3 shell of each bonding atom must be the average of $E(mol.atom, msp^3)$ for two different values of s:

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2}$$
(15.28)

In this case, $E_T(atom-atom,msp^3)$, the energy change of each $atom\ msp^3$ shell with the formation of each atom-atom-bond MO, is average for two different values of s:

15
$$E_T \left(atom - atom, msp^3 \right) = \frac{E_T \left(atom - atom \left(s_1 \right), msp^3 \right) + E_T \left(atom - atom \left(s_2 \right), msp^3 \right)}{2}$$
 (15.29)

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each C = C double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each C - H bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the

linear combination of 75% H_2 -type ellipsoidal MO and 25% $C2sp^3$ HO as given by Eq. (13.439). However, $E_T(atom-atom,msp^3)$ of the C-H-bond MO is given by $0.5E_T(C=C,2sp^3)$ (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for C-H that is lowered in energy due to the aromatic character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of H_2 -type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 10 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO 15 comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general, E_T (atom – atom, msp^3), the energy change of each atom msp^3 shell with the formation of 20 each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_{T}\left(atom - atom, msp^{3}\right) = \sum_{n=1}^{N} c_{s_{n}} E_{T}\left(atom - atom\left(s_{n}\right), msp^{3}\right)$$
 (15.30)

where c_{s_n} is the multiple of the BO of s_n . The radius r_{msp^3} of the atom msp^3 shell of each bonding atom is given by the Coulombic energy using the initial energy $E_{Coulomb}$ (atom, msp^3) and E_T (atom – atom, msp^3), the energy change of each atom msp^3 shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\varepsilon_0 a_0 \left(E_{Coulonb}\left(atom, msp^3\right) + E_T\left(atom - atom, msp^3\right)\right)}$$
(15.31)

where $E_{Coulomb}(C2sp^3) = -14.825751 \ eV$. The Coulombic energy $E_{Coulomb}(mol.atom, msp^3)$ of the outer electron of the $atom \ msp^3$ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the $atom \ msp^3$ shell is given by the sum of $E_{Coulomb}(mol.atom, msp^3)$ and E(magnetic) (Eq. (15.20)). $E_T(atom - atom, msp^3)$, the energy change of each $atom \ msp^3$ shell with the formation of the atom-atom-bond MO is given by the difference between $E(mol.atom, msp^3)$ and $E(atom, msp^3)$ given by Eq. (15.21). Using Eq. (15.23) for $E_{Coulomb}(C, 2sp^3)$ in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

15 Table 15.2. The final values of r_{C2sp^3} , $E_{Coulomb}(C2sp^3)$, and $E(C2sp^3)$ and the resulting $E_r(C^{BO}_{-C},C2sp^3)$ of the MO comprising a linear combination of H_2 -type ellipsoidal MOs and corresponding HOs of single or mixed bond order where c_{s_n} is the multiple of the bond order parameter $E_T(atom-atom(s_n),msp^3)$ given in Table 15.1.

Table	15.	1					.55			
MO	s	$c_{s_{l}}$	s	C_{s_2}	S	c_{s_3}	r (a)	$F = (C2sn^3)$	E(C2-3)	(BO)
Bond	1	-31	2	32	3	83	C2sp3 (*0)	$E_{Coulomb}\left(C2sp^3\right)$ (eV)	(eV)	$E_T \left(C - C, C2sp^3 \right)$
Order							Final	Final	Final	(eV)
(BO)									i iidi	
1/2I	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/211	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
I +	1	0.5	2	0.2	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/211				5						
1/2II	2	0.2	1	0.2	2	0.2	0.87363	-15.57379	-15.38293	-0.74804
+ (I +		5		5		5				
II)										
3/4II	2	0.7	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
		5								
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
	. 1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
III	_									
I +	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
IV II +	2	0.5	3	0.5	•					
Ш	2	0.5	3	0.5	0	.0	0.84115	-16.17521	-15.98435	-1.34946
II+	2	0.5	4	0.5	0	0	0.00040	16.40004		
IV	2	0.5	~	0.5	U	U	0.82948	-16.40286	-16.21200	-1.57711
m +	3	0.5	4	0.5	0	0	0.81871	-16.61853	16 40767	1 70070
IV ·	-	0.5	•	0.5	v	v	0.010/1	-10.01033	-16.42767	-1.79278
IV+	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043
IV						-		10.0.015	10.05552	-2.02043

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as 5 carbon superimposes linearly. In general, the radius r_{mol2sp^3} of the $C2sp^3$ HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering $\sum E_{T_{mol}} (MO, 2sp^3)$, the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb}\left(C, 2sp^{3}\right) + \sum E_{T_{mol}}\left(MO, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e^{1}4.825751 \ eV + \sum \left|E_{T_{mol}}\left(MO, 2sp^{3}\right)\right|\right)}$$
(15.32)

The Coulombic energy $E_{Coulomb}$ (mol.atom, msp³) of the outer electron of the atom msp³ shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E(mol.atom, msp^3)$ of the outer electron of the atom msp^3 shell is given by the sum of $E_{Coulomb}$ (mol.atom, msp³) and E(magnetic) (Eq. (15.20)).

For example, the $C2sp^3$ HO of each methyl group of an alkane contributes $10 -0.92918 \, eV$ (Eq. (14.513)) to the corresponding single C-C bond; thus, the corresponding $C2sp^3$ HO radius is given by Eq. (14.514). The $C2sp^3$ HO of each methylene group of C_nH_{2n+2} contributes $-0.92918 \, eV$ to each of the two corresponding C-C bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$r_{alkaneC_{methylers} 2:p^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb} \left(C, 2sp^{3} \right) + \sum_{T_{allane}} \left(methylene \ C - C, 2sp^{3} \right) \right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + e0.92918 \ eV + e0.92918 \ eV \right)}$$

$$= 0.81549a_{0}$$
(15.33)

$$E_{Coulomb}\left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}\left(0.81549a_{0}\right)} = -16.68412 \ eV \tag{15.34}$$

$$E\left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}\left(0.81549a_{0}\right)} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(0.84317a_{0}\right)^{3}} = -16.49325 \ eV \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to $C2sp^3$ HOs to form MOs are energy matched to the $C2sp^3$ HOs. Thus, the radius and the 20 energy parameters of a bonding heteroatom are given by the same equations as those for

 $C2sp^3$ HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO, $r_{Atom.HO.AO}$, $E_{Coulomb}$ (mol.atom, msp^3), and $E(C_{mol}2sp^3)$ are calculated using $\sum E_{T_{group}}$ (MO,2sp³), the total energy donation to each bond with which an atom participates in bonding corresponding to the values of E_r ($C^{BO}_{-C,C2sp^3}$) of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}$ (mol.atom, msp³), and $E(C_{mol}2sp^3)$ calculated using the values of $E_T(C_{-C,C2sp^3}^{BO})$ given in Tables 15.1 and 15.2.

		_		_									4:	58															
26	25	24	23	22	21	20	19	18	17	16	15	14	13	13	11	10	9	8	7	6	5	4	S	2	1	ion	Designat	ation	Hybridiz
-2.02043	-0.92918	-1.13379	-1.79278	-0.85035	-0.72457	-1.57711	-0.64574	-1.56513	-0.82688	-0.5669	-0.72457	-0.46459	-1.3725	-1.34946	-0.46459	-1.14485	-1.13379	-0.54343	-0.92918	-0.85034	-0.72457	-0.56689	-0.46459	-0.36229	0				$E_T\left(C-C,C2sp^3\right)$
0	-0.92918	-0.72457	0	-0.85035	-0.92918	0	-0.92918	0	-0.72457	-0.92918	-0.72457	-0.92918	0	0	-0.82688	0	0	-0.54343	0	0	0	0	0	0	0		_		$E_T\bigg(C-C,C2sp^3\bigg)\bigg E_T\bigg(C-C,C2sp^3\bigg)\bigg E_T\bigg(C-C,C2sp^3\bigg)\bigg E_T\bigg(C-C,C2sp^3\bigg)\bigg E_T\bigg(C-C,C2sp^3\bigg)\bigg E_T\bigg(C-C,C2sp^3\bigg)\bigg E_T\bigg(C-C,C2sp^3\bigg)\bigg $
0	0	0	0	0	0	0	0	0	0	O	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_T\left(C-C,C2sp^3\right)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_{\tau}\left(C-C,C2sp^{3}\right)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_T \left(C - C, C2sp^3 \right)$
0.80765	0.81549	0.81549	0.81871	0.82327	0.82562	0.82948	0.82959	0.83008	0.83078	0.8336	0.836	0.83885	0.83995	0.84115	0.84418	0.85193	0.85252	0.85503	0.86359	0.86793	0.87495	0.88392	0.88983	0.89582	0.91771			Final	Atom.HO.AO
-16.84619	-16.68412	-16.68411	-16.61853	-16.52645	16.47951	-16.40286	-16.40067	-16.39089	-16.37721	-16.32183	-16.2749	-16.21952	-16.19826	-16.17521	-16.11722	-15.9706	-15.95955	-15.91261	-15.75493	-15.6761	-15.55033	-15.39265	-15.29034	-15.18804	-14.82575	רוחמו	: (e	S	$E_{Coulomb}$ (mol.atom, msp ³) $E(C_{mol}2sp^3)$
-16.65532	-16.49325	-16.49325	-16.42767	-16.33559	-16.28865	-16.212	-16.20981	-16.20002	-16.18634	-16.13097	-16.08404	-16.02866	-16.00739	-15.98435	-15.92636	-15.77974	-15.76868	-15.72175	-15.56407	-15.48523	-15.35946	-15.20178	-15.09948	-14.99717	-14.63489		Final	(eV)	$) E(C_{max}2sp^3)$

_	$\overline{}$		$\overline{}$	_	_	_	45	" —			_																
2	\$;	40	48	47	46	đ	‡	2 2	A3 6	45	4	40	39	38	رِ	77	36	35	34	33	32	31	ي	3	20 1	28	- //
-1./92/8	1 70777	-112370	-0.82688	-0.46459	-1.1338	-0.85034	-1.34946	1 7404	0.525.0-	-0 0000 O	-0.82688	-0.92918	-0.54343	-0.92918	1.047/.0-	0.02450	-0.82688	-0.72457	-0.85035	-0.64574	-0.46459	-1.34946	-1.13379	0.3007	0995 U	25028 0-	-1.13379
-0.92918	1.155/9	1 12270	-1 34946	-0.85035	-0.92918	-0.54343	-0.64574	-0.54343	-0.92918	0.72310	-D 62018	-0.85034	-0.54343	-0.72457	-0.92918	-0.72437	D 77457	J) 72457	-0.5669	-0.85034	-0.92918	-0.92918	-1.13379	-0./243/	-0.63053	0 95035	-0.92918
-0.92918	-1.133/9	0.7270	01000 0	-0.85035	-0.92918	-0.60631	-0.92918	-0.5669	-0.92918	-0.32518	0.00007	-0.85027	-0.5669	-0.92918	-0.92918	-0.92918	0.727.0-	0.727.0	81000 0-	75038 U-	-0.92918	0	0	-0.92918	-0.46439	2400	0
0	0	o		-0 92918	0	-0.92918	0	-0.92918	0	C		0	-0 92918	0	0	0	, c				0	0	0	0	0		0
0	0	0			0	0	. 0	0	0	0	0		>	0	0	0	0	0	ò			0	0	0	0		
0.73637	0.74646	0.75877	0.73924	0 7603	0.7636	0.76631	0.76652	0.76801	0.77247	0.77699	0.77945	0.76133	0.70162	0.78155	0.78155	0.78617	0.79085	0.79232	0.79232	0.79340	0.755.10	0.70476	0.79597	0.78916	0.80076	0.80561	2,225
-18.47690	-18.22712	-17.93128	-17.92022	.,,,,,,,,	-17 81791	-17.75502	-17.75013	-17.71561	-17.6133	-17.51099	-17.45561	-17.40869	17.70007	-17 40860	-17.40868	-17.30638	-17.20408	-17.17218	-17.17217	-17.14871	-17.1044	12 104	-17.09334	-17.04641	-16.99104	-16.88872	
-18.28604	-18.03626	-17.74041	-17.72936	CO/70./1-	-17 62706	-17.56415	-17.55927	-17.52475	-17.42244	-17.32013	-17.26475	-17.21783	C9/17/12	17 21702	-17.21782	-17.11552	-17.01322	-16.98132	-16.98131	-16.95784	-16.91353	-10.70240	16,000,40	-16.85554	-16.80018	-16.69786	

Table 15.3.B. The final values of $r_{Atom.HO.AO}$, $E_{Coulomb}$ (mol.atom, msp³), and $E(C_{mol}2sp^3)$ calculated for heterocyclic groups using the values of $E_T(C^{BO}_T(C^{BO}_T))$ given in Tables 15.1 and 15.2.

													91														
26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	Designation	Atom Hybridization
-1.13379	-0.85034	-0.85034	-0.92918	-0.85034	-0.54343	-0.85035	-0.85035	-1.13379	-0.85034	-0.85035	-1.13379	-1.13379	-0.92918	-0.85035	-0.92918	-0.92918	-0.72457	-0.46459	-0.60631	-1.13379	-0.54343	-0.92918	-0.72457	-0.56690	0		$E_{\mathbf{r}}\left(\overset{\boldsymbol{\omega}}{C}-C,C2sp^{1}\right)$
-0.92918	-0.54343	-0.54343	-0.92918	-0.28345	-0.54343	-0.56690	-0.54343	-1.13380	-0.85034	-0.85035	-0.92918	-0.72457	-0.92918	-0.85035	-0.72457	-0.60631	-0.72457	-0.92918	-0.60631	0	-0.54343	0	0	0	0		$E_{r}\left(C-C,C2sp^{3}\right)$
-0.92918	-0.60631	-0.56690	-0.92918	-0.54343	-0.56690	-0.92918	0.00000	0	-0.56690	-0.46459	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T\left(C-C,C2sp^3\right)$ $E_T\left(C-C,C2sp\right)$
0	-0.92918	-0.92918	0	-0.92918	-0.92918	0	-0.92918	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T\left(C-C,C2sp^3\right)$
0 .	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_{\tau}\bigg(C-C,C2sp^3\bigg)$
0.76360	0.76631	0.76801	0.77247	0.78050	0.78155	0.79232	0.79340	0.79597	0.79597	0.80076	0.80561	0.81549	0.81549	0.82327	0.82562	0.83159	0.83600	0.83885	0.84833	0.85252	0.85503	0.86359	0.87495	0.88392	0.91771	Final	P _{Atom.HO.AO}
-17.81791	-17.75502	-17.71560	-17.61330	-17.43216	-17.40869	-17.17218	-17.14871	-17.09334	-17.09334	-16.99103	-16.88873	-16.68412	-16.68411	-16.52644	-16,47951	-16.36125	-16.27490	-16.21953	-16.03838	-15.95954	-15.91261	-15.75493	-15.55033	-15.39265	-14.82575	(cV) Final	Ecculosab (mol atom, msp³)
-17.62704	-17.56416	-17.52474	-17.42243	-17.24130	-17.21783	-16.98132	-16.95785	-16.90248	-16.90247	-16.80017	-16.69786	-16.49325	-16.49325	-16.33558	-16.28864	-16.17038	-16.08404	-16.02866	-15.84752	-15.76868	-15.72175	-15.56407	-15,35946	-15.20178	-14.63489	(eV) Final	$E\left(C_{mol}2sp^3\right)$

Γ	_	Ŧ	_	7		7	_	_
	ت		23	36	6	30	ļ	7.7
	-1.13379		-1.13380	1 13300	-0.40439	036360		17770
71.000	-1 13379		-1.13379		-0.85035		-1.13	1 13700
-1.10077	96551 1-	4:727	5000		-0.85035		-0.72457	
		c			-0.92918		0	
0		c		•	0		0	
0.74646		0.75493		47667.0	0.2600	0.7000	02525	
-18.22713		-18.02252		-17.9Z0ZZ	12	-17.81791	10000	
-18.03627	17.00100	17 83166		-17.72935		-17.62705		

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant k' 5 (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each H_2 -type-ellipsoidal-MO in terms of the central force of the foci. Then, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2 , $-31.63536831 \, eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal 10 MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis a as it only parameter. The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy, $E_T(H,MO)$, is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus $E_T(AO/HO)$:

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO)$$
 (15.36)

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}-1\right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + E_{T}(AO/HO)$$
(15.37)

where n_1 is the number of equivalent bonds of the MO, c_1 is the fraction of the H_2 -type ellipsoidal MO basis function of a chemical bond of the group, c_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and $E_T(AO/HO)$ is the total energy comprising the difference of the energy E(AO/HO) of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component $\Delta E_{H_2MO}(AO/HO)$ due to the AO or HO's charge donation to the MO.

$$E_{T}(AO/HO) = E(AO/HO) - \Delta E_{H,MO}(AO/HO)$$
(15.38)

As specific examples given in previous sections, $E_T(AO/HO)$ is one from the group of

$$E_{T}(AO / HO) = E(O2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV};$$

$$E_{T}(AO / HO) = E(N2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E_{T}(AO / HO) = E(C,2sp^{3}) = -14.63489 \text{ eV};$$

5
$$E_T(AO/HO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295 \text{ eV};$$

 $E_T(AO/HO) = E(ionization; C) + E(ionization; C^+);$

$$E_T(AO/HO) = E(C_{ethane}, 2sp^3) = -15.35946 \ eV;$$

$$E_T(AO/HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3);$$

$$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C=C,2sp^3) = -14.63489 eV - (-2.26758 eV);$$

10
$$E_T(AO/HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \text{ eV};$$

$$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C = C,2sp^3) = -14.63489 eV - (-3.13026 eV);$$

$$E_T(AO/HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$$

$$E_T(AO/HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-1.13379 \text{ eV}), \text{ and}$$

$$E_T(AO/HO) = E(C_{alkane}, 2sp^3) = -15.56407 eV$$
.

To solve the bond parameters and energies,
$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1C_2 a}} = \sqrt{\frac{aa_0}{2C_1C_2}}$$
 (Eq.

(15.2)) is substituted into $E_{\tau}(u_{1}MO)$ to give

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2} \left(2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}(AO/HO)$$

The total energy is set equal to $E(basis\ energies)$ which in the most general case is given by

the sum of a first integer n_1 times the total energy of H_2 minus a second integer n_2 times the total energy of H, minus a third integer n_3 times the valence energy of E(AO) (e.g. $E(N) = -14.53414 \ eV$) where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....

 $E(basis\ energies) = n_1(-31.63536831\ eV) - n_2(-13.605804\ eV) - n_3E(AO)$ (15.40) In the case that the MO bonds two atoms other than hydrogen, $E(basis\ energies)$ is n_1 times the total energy of H_2 where n_1 is the number of equivalent bonds of the MO and the energy of H_2 , $-31.63536831\ eV$, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

10
$$E(basis\ energies) = n_1(-31.63536831\ eV)$$
 (15.41)

 $E_T(H_1MO)$, is set equal to $E(basis\ energies)$, and the semimajor axis a is solved. Thus, the semimajor axis a is solved from the equation of the form:

$$-\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}\left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}-1\right]+E_{T}\left(AO/HO\right)=E(basis\ energies)\ (15.42)$$

The distance from the origin of the H_2 -type-ellipsoidal-MO to each focus c', the internuclear 15 distance 2c', and the length of the semiminor axis of the prolate spheroidal H_2 -type MO b=c are solved from the semimajor axis a using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group, E_T (MO), is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and E_T (atom – atom, msp³.AO), the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40), E_T (MO) is

$$E_T(MO) = E(basis\ energies) + E_T(atom - atom, msp^3.AO)$$
 (15.43)

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy \overline{E}_{osc} is the sum of the Doppler, \overline{E}_{D} , and 25 average vibrational kinetic energies, \overline{E}_{Kvib} :

$$\overline{E}_{osc} = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(E_{hv} \sqrt{\frac{2\overline{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.44)

where n_1 is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and μ is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to \overline{E}_D is determined by the force between the central field and the electrons in the transition state. The force and its derivative are given by

$$f\left(R\right) = -c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.45}$$

and

$$f'(a) = 2c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}$$
 (15.46)

10 such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{10}C_{20}e^2}{4\pi\epsilon_0 R^3}}{m_e}}$$
(15.47)

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state, c_{RO} is the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{RO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules and 9 for an independent triplet bond. C_{1o} is the fraction of the H_2 -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. 20 Typically, $C_{1o} = C_1$ and $C_{2o} = C_2$. The kinetic energy, E_K , corresponding to \overline{E}_D is given by Planck's equation for functional groups:

$$\bar{E}_{\kappa} = \hbar \omega = \hbar \sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}$$

$$m_{\varepsilon}$$
(15.48)

The Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_{D} \cong E_{h\nu} \sqrt{\frac{2\overline{E}_{K}}{m_{e}c^{2}}} = E_{h\nu} \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{0}R^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}$$

$$(15.49)$$

 \overline{E}_{osc} given by the sum of \overline{E}_{D} and \overline{E}_{Kvlb} is

$$\overline{E}_{osc}(group) = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(E_{hv} \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{\frac{m_e}{m_e}}} + E_{vib} \right) \tag{15.50}$$

 $E_{h\nu}$ of a group having n_1 bonds is given by E_T (MO)/ n_1 such that

5
$$\overline{E}_{osc} = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(E_T \left(\omega_0 \right) / n_1 \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.51)

 E_{T+osc} (Group) is given by the sum of E_{T} (MO) (Eq. (15.42)) and \bar{E}_{osc} (Eq. (15.51)):

$$E_{T+asc}$$
 (Group)= E_{T} (MO)+ \bar{E}_{osc}

$$= \left(-\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}} - 1}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}} - 1} \right] \right)$$

$$= \left(+E_{T}\left(AO / HO\right) + E_{T}\left(atom - atom, msp^{3}.AO\right) \right)$$

$$\left[-\frac{1}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{\frac{aa_{0}}{m_{e}}} + n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right]$$

$$= \left(E(basis\ energies) + E_{\tau}\left(atom - atom, msp^{3}.AO\right)\right) 1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right) + n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

The total energy of the functional group $E_T(group)$ is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms, $E(basis\ energies)$, the change in the energy of the AOs or HOs upon forming the bond $(E_T(atom-atom,msp^3.AO))$, the energy of oscillation in the transition state, and the change in magnetic energy with bond formation, E_{mag} . From Eq. (15.52), the total energy of the group $E_T(group)$ is

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right]$$

$$+n_{1}\bar{E}_{Kvib} + E_{mag}$$
(15.53)

The change in magnetic energy E_{mag} which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$E_{mag} = c_3 \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = c_3 \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.54)

where r^3 is the radius of the atom that reacts to form the bond and c_3 is the number of electron pairs.

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}$$

$$(15.55)$$

The total bond energy of the group E_D (Group) is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of $c_4 E_{initial}$ ($c_4 AO/HO$) and $c_5 E_{initial}$ ($c_5 AO/HO$):

$$E_{D}(Group) = -\left(E(basis\ energies) + E_{T}\left(atom - atom, msp^{3}.AO\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}}c^{2}}}\right]\right) + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r_{n}^{3}} - \left(c_{4}E_{Initial}\left(AO/HO\right) + c_{5}E_{Initial}\left(c_{5}AO/HO\right)\right)$$

$$(15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the $C2sp^3$ HO such that

$$E(AO/HO) = -14.63489 eV (15.57)$$

5 For examples of E_{mag} from previous sections:

$$E_{mag}\left(C2sp^{3}\right) = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{\left(0.91771a_{o}^{3}\right)^{3}} = c_{3}0.14803 \ eV$$
 (15.58)

$$E_{mag}\left(O2p\right) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441 \ eV \tag{15.59}$$

$$E_{mag}(N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{\left(0.93084a_0\right)^3} = c_3 0.14185 \ eV$$
 (15.60)

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the H_2 -type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor c_2 of a H_2 -type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:
$$c_2 = 1$$
 (15.61)

20 (ii) the ratio that is less than one of $13.605804 \, eV$, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom, $E_{Coulomb}$ (MO.atom, msp³) given by Eqs. (15.19) and (15.31-15.32). For $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right>$ 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}$$
(15.62)

For $\left| E_{Coulomb} \left(MO.atom, msp^3 \right) \right| < 13.605804 \ eV$:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}}{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}{13.605804\ eV}$$
(15.63)

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, E(valence), of the participating AO or HO of the atom where E(valence) is 10 the ionization energy or $E(MO.atom, msp^3)$ given by Eqs. (15.20) and (15.31-15.32). For $|E(valence)| > 13.605804 \ eV$:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{|E(valence)|}$$
(15.64)

For |E(valence)| < 13.605804 eV:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{|E(valence)|}{13.605804 \ eV}$$
(15.65)

15

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom, $E_{Coulomb}$ (MO.atom, msp³) given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, E(valence), of the participating AO or HO of a second atom to which the first is energy matched where E(valence) is the

ionization energy or $E(MO.atom, msp^3)$ given by Eqs. (15.20) and (15.31-15.32). For $E_{Conlomb}(MO.atom, msp^3) > E(valence)$:

$$c_2 = \frac{|E(valence)|}{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}$$
(15.66)

For $|E_{Coulomb}(MO.atom, msp^3)| < E(valence)$:

$$c_2 = \frac{\left| E_{Coulomb} \left(MO.atom, msp^3 \right) \right|}{\left| E(valence) \right|} \tag{15.67}$$

(v) the ratio that is less than one of the magnitude of the valence-level energies, $E_n(valence)$, of the AO or HO of the nth participating atom of two that are energy matched where E(valence) is the ionization energy or $E(MO.atom, msp^3)$ given by Eqs. (15.20) and 10 (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \tag{15.68}$$

(vi) the factor that is the ratio of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.68); alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \tag{15.69}$$

20

(vii) the factor that is the product of the hybridization factor $c_2(1)$ of the valence AO or HO of a first atom and the hybridization factor $c_2(2)$ of the valence AO or HO of a second atom to which the first is energy matched where $c_2(n)$ is given by Eqs. (15.62-15.69);

alternatively c_2 is the hybridization factor $c_2(1)$ of the valence AOs or HOs a first pair of atoms and the hybridization factor $c_2(2)$ of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) (15.70)$$

5 The hybridization factor c_2 corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then C_2 corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors c_2 and C_2 of a H_2 -type ellipsoidal MO of Eq. 10 (15.51) given in following sections are

$$c_{2}(C2sp^{3}HO \text{ to } F) = \frac{E(C,2sp^{3})}{E(F)}c_{2}(C2sp^{3}HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}}(0.91771) = 0.77087;$$

$$C_{2}(C2sp^{3}HO \text{ to } Cl) = \frac{E(Cl)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.81317;$$

$$C_{2}(C2sp^{3}HO \text{ to } Br) = \frac{E(Br)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.74081;$$

$$C_{2}(C2sp^{3}HO \text{ to } I) = \frac{E(I)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.65537;$$

$$15 \quad c_{2}(C2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.85395;$$

$$c_{2}(H \text{ to } 1^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(S3p \text{ to } H) = \frac{E(S)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965;$$

$$20 \quad C_{2}(C2sp^{3}HO \text{ to } S) = \frac{E(S)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965;$$

$$c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3HO) = \frac{E(O)}{E(S)}c_2(C2sp^3HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771);$$

$$= 1.20632$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045;$$

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}\left(0.85045\right) = 0.66951;$$

$$C_{2}(S3sp^{3} \text{ to O to } C2sp^{3}HO) = \frac{E(S, 3sp^{3})}{E(O, 2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771);$$

$$= 0.77641$$

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771);$$

$$= 0.85987$$

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2$$
 (benzeneC2sp³HO)= c_2 (benzeneC2sp³HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$;

$$c_{2}(arylC2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.85252)$$

$$= 0.70320$$

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252) ,$$

$$= 0.84665$$

and

10

5

$$C_2 \left(S3p \text{ to aryl-type } C2sp^3 HO \right) = \frac{E\left(S, 3p \right)}{E\left(C, 2sp^3 \right)} = \frac{-10.36001 \, eV}{-15.76868 \, eV} = 0.65700 \, .$$

MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a B atom and the nucleus of a A atom comprise the foci of each H_2 -type ellipsoidal MO of an A-B bond. The parameters of the point of intersection of each H_2 -type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{15.71}$$

The radius of the A shell is r_A , and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_{A} = \left(a - c'\right) \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a}\cos\theta'} \tag{15.72}$$

The polar angle θ' at the intersection point is given by

$$\theta' = \cos^{-1}\left(\frac{a}{c'}\left((a-c')\frac{1+\frac{c'}{a}}{a_0}-1\right)\right)$$
 (15.73)

Then, the angle θ_{AAO} the radial vector of the A AO makes with the internuclear axis is

$$\theta_{AAO} = 180^{\circ} - \theta' \tag{15.74}$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle $\omega t = \theta_{H_2MO}$ between the internuclear axis and the point of intersection of each H_2 -type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO} \tag{15.75}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_a \sin \theta_{AAO}}{h} \tag{15.76}$$

The distance d_{H_2MO} along the internuclear axis from the origin of H_2 -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_1MO} = a\cos\theta_{H_1MO} \tag{15.77}$$

The distance d_{AAO} along the internuclear axis from the origin of the A atom to the point of 5 intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H.MO} ag{15.78}$$

BOND ANGLES

Further consider an ACB MO comprising a linear combination of C-A-bond and C-B10 bond MOs where C is the general central atom. A bond is also possible between the A and B atoms of the C-A and C-B bonds. Such A-B bonding would decrease the C-A and C-B bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the $\angle ACB$ bond angle is determined by the condition that the total energy of the H_2 -type ellipsoidal MO between the terminal A and B atoms is zero. The force constant k' of a H_2 -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.79}$$

where C_1 is the fraction of the H_2 -type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal A - H (A is H or other atom) and 1 20 otherwise and C_2 is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus c' of the A - B ellipsoidal MO is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.80)

25 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.81}$$

The length of the semiminor axis of the prolate spheroidal A - B MO b = c is given by Eq. (15.4).

The component energies and the total energy, $E_T(n,MO)$, of the A-B bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of H_2 except 5 that the terms based on charge are multiplied by c_{BO} , the bond-order factor which is 1 for a single bond and when the MO comprises n_1 equivalent single bonds as in the case of functional groups. c_{BO} is 4 for an independent double bond as in the case of the CO_2 and NO_2 molecules. The kinetic energy term is multiplied by c'_{BO} which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by c_1 , 10 the fraction of the H_2 -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal A-H (A is H or other atom) and 1 otherwise. The electron energy terms are further multiplied by c'_2 , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when A-B comprises atoms other than H, 15 E_T (atom – atom, msp³.AO), the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give E_T (μ_1MO):

$$E_{T}(H_{2}MO) = \frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[c_{1}c'_{2} \left(2c_{BO} - c'_{BO} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_{T} \left(atom - atom, msp^{3}.AO \right)$$
(15.82)

The radiation reaction force in the case of the vibration of A-B in the transition state 20 corresponds to the Doppler energy, E_D , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the A-B MO is given by the sum of $E_T(\mu_{2,MO})$ (Eq. (15.82)) and \overline{E}_{osc} given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy $E_T(A-B)$ of the A-B MO including the Doppler term is

$$E_{T}(A-B) = \begin{bmatrix} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[c_{1}c'_{2}\left(2c_{BO} - c'_{BO}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'} - 1\right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \right] \\ \left[1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}}a^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c'_{2}e^{2}}{8\pi\varepsilon_{o}}a^{3} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{o}}(a+c')^{3}}{\mu}} \\ (15.83)$$

where C_{1o} is the fraction of the H_2 -type ellipsoidal MO basis function of the oscillatory transition state of the A-B bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise, C_{2o} is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the A-B ellipsoidal MO is zero, $E_T(A-B)$ given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$10 \quad 0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}'\left(2c_{BO} - c_{BO}'\frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \end{bmatrix}$$

$$= \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}'\left(2c_{BO} - c_{BO}'\frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \right] + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c_{2}'e^{2}}{8\pi\varepsilon_{0}}a^{3}}{e^{3} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{0}}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)^{3}}} \right]}$$

$$= \begin{bmatrix} 1 - \sqrt{\frac{aa_{0}}{2h\sqrt{\frac{aa_{0}}{a}}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}}} \\ \frac{a}{h}\sqrt{\frac{aa_{0}}{2c_{1}C_{2}}} \end{bmatrix} + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}} \end{bmatrix}} + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}}} \end{bmatrix} + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}}}$$

$$= \begin{bmatrix} 1 - \sqrt{\frac{aa_{0}}{a}}{2h\sqrt{\frac{aa_{0}}{a}}}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}}} \\ \frac{aa_{0}}{2c_{1}C_{2}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}} \end{bmatrix}} + \frac{1}{2}\hbar\sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{2c_{1}C_{2}}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}} + \sqrt{\frac{aa_{0}}{a}}} \\ \frac{aa_{0}}{a$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

15
$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi \varepsilon_0 a^3}$$
 (15.85)

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3}$$
 (15.86)

The nuclear repulsion force and its derivative are given by

$$f\left(a+c'\right) = \frac{e^2}{8\pi\varepsilon_o\left(a+c'\right)^2} \tag{15.87}$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o(a+c')^3}$$
 (15.88)

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_1c_2'e^2}{4\pi\varepsilon_0a^3} - \frac{e^2}{8\pi\varepsilon_0(a+c')^2}}$$
(15.89)

Since both terms of $\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$ are small due to the large values of a and c', to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}'\left(2 - \frac{a_{0}}{a}\right)\ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1\right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \\ \left[\frac{1 + \sqrt{\frac{c_{1}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{2\hbar\sqrt{\frac{c_{1}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{m_{e}}} + \frac{1}{2}\hbar\sqrt{\frac{\frac{c_{1}e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{e^{2}}{8\pi\varepsilon_{o}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)}}{\mu}}\right] (15.90)$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the A-B MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor c_2 of a given atom in the determination of c_2' for calculating the zero of the total A-B bond energy is typically given by Eqs. (15.62-15.65). In the case of a H-H terminal bond of an alkyl or alkenyl group, c_2' is typically the ratio of c_2 of Eq. (15.62) for the H-H bond which is one and c_2 of the carbon of the corresponding C-H bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \, eV}{E_{Coulomb} \left(C - H \, C2sp^3\right)}$$
(15.91)

In the case of the determination of the bond angle of the ACH MO comprising a linear combination of C-A-bond and C-H-bond MOs where A and C are general, C is the central atom, and c_2 for an atom is given by Eqs. (15.62-15.70), c_2' of the A-H terminal bond is typically the ratio of c_2 of the A atom for the A-H terminal bond and c_2 of the C atom of the corresponding C-H bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3))}$$
(15.92)

In the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of C-O-bond and O-H-bond MOs where C, O, and H are carbon, 10 oxygen, and hydrogen, respectively, c'_2 of the C-H terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the $C2sp^3$ HO.

In the determination of the hybridization factor c_2' of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy, $E_{Coulomb} \left(MO.atom, msp^3 \right)$, or the energy, $E\left(MO.atom, msp^3 \right)$, 15 the radius $r_{A-B.AorBsp^3}$ of the A or B AO or HO of the heteroatom of the A-B terminal bond MO such as the $C2sp^3$ HO of a terminal C-C bond is calculated using Eq. (15.32) by considering $\sum E_{T_{mol}} \left(MO.2sp^3 \right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy $E_{Coulomb} \left(MO.atom, msp^3 \right)$ of the outer electron of the atom msp^3 shell is given by Eq. (15.19).

- In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy $E(MO.atom, msp^3)$ of the outer electron of the $atom\ msp^3$ shell is given by the sum of $E_{Coulomb}(MO.atom, msp^3)$ and E(magnetic) (Eq. (15.20)).
- In the specific case of the terminal bonding of two carbon atoms, the c_2 factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy $E_{Coulomb} \left(C C C 2 s p^3\right)$ of the outer electron of the $C 2 s p^3$ shell given by Eq. (15.19) with the

radius $r_{C-C\ C2sp^3}$, of each $C2sp^3$ HO of the terminal C-C bond calculated using Eq. (15.32) by considering $\sum E_{T_{mol}} \left(MO, 2sp^3 \right)$, the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal C-C bond. 5 The corresponding $E_T \left(atom-atom, msp^3.AO \right)$ in Eq. (15.90) is $E_T \left(C-C\ C2sp^3 \right) = -1.85836\ eV$.

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus, c'_2 is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

10
$$c_2' = \frac{1}{2} \left(c_2' \left(atom \ 1 \right) + c_2' \left(atom \ 2 \right) \right)$$
 (15.93)

In the exemplary cases of C-C, O-O, and N-N where C is carbon:

$$c_{2}' = \frac{1}{2} \left(\frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-A_{1}AO/HO}}} + \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-A_{2}AO/HO}}} \right)$$

$$= \frac{1}{2} \left(\frac{13.605804 \ eV}{E_{Coulomb} \left(A - A.A_{1}AO/HO \right)} + \frac{13.605804 \ eV}{E_{Coulomb} \left(A - A.A_{2}AO/HO \right)} \right)$$
(15.94)

In the exemplary cases of C - N, C - O, and C - S,

$$c_2' = \frac{1}{2} \left(\frac{13.605804 \ eV}{E_{Coulomb} \left(C - B \ C2sp^3 \right)} + c_2 \left(C \ to \ B \right) \right)$$
 (15.95)

where C is carbon and $c_2(C \text{ to } B)$ is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group. For these cases, the corresponding $E_T(atom-atom,msp^3.AO)$ term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

20
$$E_{T}(C - O C2sp^{3}.O2p) = -1.44915 eV;$$
 $E_{T}(C - O C2sp^{3}.O2p) = -1.65376 eV;$ $E_{T}(C - N C2sp^{3}.N2p) = -1.44915 eV;$ $E_{T}(C - S C2sp^{3}.S2p) = -0.72457 eV;$ $E_{T}(O - O O2p.O2p) = -1.44915 eV;$ $E_{T}(O - O O2p.O2p) = -1.65376 eV;$

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$$E_{T}(N-N N2pN2p) = -1.44915 \ eV; \qquad E_{T}(N-O N2pO2p) = -1.44915 \ eV;$$

$$E_{T}(F-F F2pF2p) = -1.44915 \ eV; \qquad E_{T}(Cl-Cl Cl3pCl3p) = -0.92918 \ eV;$$

$$E_{T}(Br-Br Br4pBr4p) = -0.92918 \ eV; \qquad E_{T}(I-I I5pJ5p) = -0.36229 \ eV;$$

$$E_{T}(C-F C2sp^{3}F2p) = -1.85836 \ eV; \qquad E_{T}(C-Cl C2sp^{3}Cl3p) = -0.92918 \ eV;$$

$$E_{T}(C-Br C2sp^{3}Br4p) = -0.72457 \ eV; \qquad E_{T}(C-I C2sp^{3}J5p) = -0.36228 \ eV, \quad \text{and}$$

$$E_{T}(O-Cl O2pCl3p) = -0.92918 \ eV.$$

In the case that the terminal bond is X-X where X is a halogen atom, c_1 is one, and c_2 is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where $E_{Coulomb} \left(MO.atom, msp^3\right)$ is determined using Eq. (15.32) and $E_{Coulomb} \left(MO.atom, msp^3\right) = 13.605804 \, eV$ for X = I. The factor C_1 of Eq. (15.90) is one for all halogen atoms. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, C_2 is the hybridization factor of Eq. (15.52) given by 15 Eq. (15.70) with $c_2(1)$ being that of the halogen given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence) = -14.63489 \, eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). $E_T(atom - atom, msp^3.AO)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.44915 \, eV$, $-0.92918 \, eV$, $-0.92918 \, eV$, and $-0.33582 \, eV$ for F, Cl, Br, and I, 20 respectively.

Consider the case that the terminal bond is C-X where C is a carbon atom and X is a halogen atom. The factors c_1 and c_2 of Eq. (15.90) are one for all halogen atoms. For X=F, c_2' is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where c_2 for carbon is given by Eq. (15.62) and c_2 for fluorine matched to 25 carbon is given by Eq. (15.70) with $c_2(1)$ for the fluorine atom given by Eq. (15.68) that matches the valence energy of F ($E_1(valence) = -17.42282 \ eV$) to that of the $C2sp^3$ HO

 $(E_2(valence) = -14.63489 \ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO $(c_2(2) = 0.91771, Eq. (13.430))$. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, c_2' is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom. C_2 of the terminal-atom bond matches that used to determine the energies of the corresponding C-X-bond MO. Then, C_2 is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with $c_2(1)$ for the halogen atom given by Eq. (15.68) that matches the valence energy of X ($E_1(valence)$) to that of the $C2sp^3$ HO ($E_2(valence) = -14.63489 \ eV$, Eq. (15.25)) and to the hybridization of $C2sp^3$ HO ($c_2(2) = 0.91771$, Eq. (13.430)). $E_T(atom-atom, msp^3.AO)$ of Eq. (15.90) is the maximum for the participating atoms which is $-1.85836 \ eV$, $-0.92918 \ eV$, $-0.72457 \ eV$, and $-0.33582 \ eV$ for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is H-X corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom. The factors c_1 and c_2 of Eq. (15.90) are 0.75 for all halogen atoms. For X=F, c_2' is given by Eq. (15.69) with c_2 of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor C_2 of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I, c_2' is also given by Eq. (15.69) with c_2 of the participating carbon given by Eq. (15.62) and c_2 of the participating X atom given by $C_2 = 0.91771$ (Eq. (13.430)) since the X atom is energy matched to the $C2sp^3$ HO. In these cases, C_2 is given by Eq. (15.65) for the corresponding atom X where C_2 matches the energy of the atom X to that of H.

Using the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding A-B MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \text{cosine } \theta = s_3^2$$
 (15.96)

With $s_1 = 2c'_{C-A}$, the internuclear distance of the C-A bond, $s_2 = 2c'_{C-B}$, the internuclear distance of each C-B bond, and $s_3 = 2c'_{A-B}$, the internuclear distance of the two terminal atoms, the bond angle $\theta_{\angle ACB}$ between the C-A and C-B bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B}) cosine \theta = (2c'_{A-B})^2$$
 (15.97)

5
$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - \left(2c'_{A-B}\right)^2}{2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)}\right)$$
 (15.98)

Consider the exemplary structure $C_bC_a(O_a)O_b$ wherein C_a is bound to C_b , O_a , and O_b . In the general case that the three bonds are coplanar and two of the angles are known, say θ_1 and θ_2 , then the third θ_3 can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.99}$$

10 In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say θ_1 , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \tag{15.100}$$

ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES

15 TRIANGLE

In the general case where the group comprises three A - B bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. The $C_{3\nu}$ axis centered on B is defined as the vertical or z-axis, and any two A - B bonds form an isosceles triangle. Then, the angle of the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance $d_{origin-B}$ from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^{\circ}} \tag{15.101}$$

the height along the z-axis from the origin to the A nucleus d_{height} is given by

25
$$d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}$$
, and (15.102)

the angle θ_{ν} of each A-B bond from the z-axis is given by

$$\theta_{v} = \tan^{-1} \left(\frac{d_{\text{origin-B}}}{d_{\text{height}}} \right) \tag{15.103}$$

Consider the case where the central atom B is further bound to a fourth atom C and the B-C bond is along the z-axis. Then, the bond $\theta_{\angle ABC}$ given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_{\nu} \tag{15.104}$$

DIHEDRAL ANGLE

Consider the plane defined by a general ACA MO comprising a linear combination of two C-A-bond MOs where C is the central atom. The dihedral angle $\theta_{\angle BC/ACA}$ between the 10 ACA-plane and a line defined by a third bond with C, specifically that corresponding to a C-B-bond MO, is calculated from the bond angle $\theta_{\angle ACA}$ and the distances between the A, B, and C atoms. The distance d_1 along the bisector of $\theta_{\angle ACA}$ from C to the internuclear-distance line between A and A, $2c'_{A-A}$, is given by

$$d_1 = 2c'_{C-A}\cos\frac{\theta_{\angle ACA}}{2} \tag{15.105}$$

15 where $2c'_{C-A}$ is the internuclear distance between A and C. The atoms A, A, and B define the base of a pyramid. Then, the pyramidal angle $\theta_{\angle ABA}$ can be solved from the internuclear distances between A and A, $2c'_{A-A}$, and between A and B, $2c'_{A-B}$, using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{\left(2c'_{A-B}\right)^{2} + \left(2c'_{A-B}\right)^{2} - \left(2c'_{A-A}\right)^{2}}{2\left(2c'_{A-B}\right)\left(2c'_{A-B}\right)}\right)$$
(15.106)

20 Then, the distance d_2 along the bisector of $\theta_{\angle ABA}$ from B to the internuclear-distance line $2c'_{A-A}$, is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.107}$$

The lengths d_1 , d_2 , and $2c'_{C-B}$ define a triangle wherein the angle between d_1 and the internuclear distance between B and C, $2c'_{C-B}$, is the dihedral angle $\theta_{\angle BCIACA}$ that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1} \left(\frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right)$$
 (15.108)

SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC 5 MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the H_2 -type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy E_{mag} (e.g. given by Eq. (15.58)) for a $C2sp^3$ HO and Eq. (15.59) for an C2sp AO) was subtracted for each set

15 by Eq. (15.58)) for a $C2sp^3$ HO and Eq.(15.59) for an O2p AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (13.428)). The intercept angles are determined from Eqs.

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(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the 20 drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2 -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 C_6H_6 can be considered a linear combination of three ethylene molecules wherein a C-H bond of each CH_2 group of $H_2C=CH_2$ is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2sp}$, $(0.85252a_0)$ of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}(C_{elhylene}, 2sp^3)$ (-15.95955 eV) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E(C_{ethylene}, 2sp^3)$ (-15.76868 eV) of the outer electron of the $C2sp^3$ shell 15 is given by Eq. (14.246). $E_T(C=C,2sp^3)$ (-1.13380 eV) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the C = C-bond MO is given by the difference between $E(C_{ethylene}, 2sp^3)$ and $E(C, 2sp^3)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each 2sp3 HO of each carbon atom initially has four unpaired electrons. Thus, the 6 H atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3 -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the $C2sp^3$ HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two C2sp3 HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination of one and two diatomic H_2 -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively. 30

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2 -type ellipsoidal MO divided between the $C2sp^3$ HOs:

35
$$\begin{cases} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C) - \text{ethylene} - \text{type} - \text{bond MO} \\ \rightarrow 6(C=C) - \text{bond MO of benzene} \end{cases}$$
 (15.142)

The linear combination of each H_2 -type ellipsoidal MO with each $C2sp^3$ HO further comprises an excess 25% charge-density contribution per bond from each $C2sp^3$ HO to the C=C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C=C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C=C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C = C-bond gives rise to the $C_{benzene} 2sp^3$ HO-shell Coulombic energy $E_{Coulomb} \left(C_{benzene}, 2sp^3 \right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and c_3 of Eq. (15.42) for the

aromatic C=C-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $E_{Coulomb}\left(C_{benzene},2sp^3\right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2$$
 (benzeneC2sp³HO)= c_2 (benzeneC2sp³HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$ (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (15.142). The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene, $E_T\left(C_6H_6, C=C\right)$, is given by (6)(0.75) times $E_{T+osc}(C=C)$ (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times $E(C,2sp^3)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the C=C bonds of bond order two. Thus, the total energy of the six C=C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6},C=C\right) = (6)(0.75)E_{T+osc}\left(C=C\right) - (6)(3)E\left(C,2sp^{3}\right)$$

$$= (6)(0.75)\left(-66.05796 \ eV\right) - 18\left(-14.63489 \ eV\right)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$
(15.144)

25 The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. E_{hr} of an aromatic bond is given by $E_{T}(H_{2})$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_{2} -type MO such that

$$\bar{E}_{osc} = n_1 \left(\bar{E}_D + \bar{E}_{Kvib} \right) = n_1 \left(-31.63536831 \ eV \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two 30 given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of

the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{T}(Group) = f_{1} \left(E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) - \frac{1}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}} - \frac{1}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{m_{e}}}} + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right)$$
(15.146)

5 The total bond energy of the aromatic group E_D (Group) is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{initial}$ ($c_4 AO/HO$) and $c_5 E_{initial}$ ($c_5 AO/HO$):

$$E_{D}(Group) = -\begin{pmatrix} E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \\ -31.63536831\ eV \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}} \\ -(c_{4}E_{initial}(AO/HO) + c_{5}E_{mintal}(c_{5}AO/HO)) \end{pmatrix}$$
(15.147)

Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic 10 bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e , V_p ,

15 T, V_m , and E_T are the same as those of the hydrogen carbide radical, except that $E_T\left(C=C,2sp^3\right)=-1.13379~eV$ (Eq. (14.247)) is subtracted from $E_T\left(CH\right)$ of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T\left(atom-atom,msp^3.AO\right)=-1.13379~eV$.

The total energy of the benzene C-H-bond MO, $E_{T_{benzene}}(C-H)$, given by Eq. (14.467) is the sum of $0.5E_T$ ($C=C,2sp^3$), the energy change of each $C2sp^3$ shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), and $E_{T_{benzene}}(CH)$, the σ MO contribution given by Eq. (14.441). In the corresponding 25 generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_1=1$ and E_T (atom-atom, msp³.AO) = $\frac{-1.13379 \text{ eV}}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{max} given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond, $-E_{D_{benzene}}\binom{12}{CH}$ (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene, $E_T(C_6H_6,C-H)$, given by Eq. (14.494) 10 is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{bincom}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV}$$
 (15.148)

The total bond dissociation energy of benzene, $E_{D}(C_{6}H_{6})$, given by Eq. (14.495) is the negative

sum of
$$E_T \left(C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and $E_T \left(C_6 H_6, C - H \right)$ (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}(C_{6}H_{6}, C = C) + E_{T}(C_{6}H_{6}, C - H)\right)$$

$$= -\left((-33.83284 \ eV) + (-23.42724 \ eV)\right)$$

$$= 57.2601 \ eV$$
(15.149)

15 Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 25 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

	<u>, </u>
Functional Group	Group Symbol
CC (aromatic bond)	3e C=C
CH (aromatic)	· CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and

experimental values [1].

Parameter	C = C Group	CH Group
$a\left(a_{_{0}}\right)$	1.47348	1.60061
$c'(a_0)$	1.31468	1.03299
Bond Length $2c'(\Box)$	1.39140	1.09327
Exp. Bond Length	1.399 (benzene)	1.101 (benzene)
b,c $\left(a_{_{0}}\right)$	0.66540	1.22265
e	0.89223	0.64537

5 Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	C=C Group	CH Group
f_1	0.75	1
$n_{\mathbf{l}}$	2	1
n_2	0	0
n ₃	0	0
C_1	0.5	0.75
C_2	0.85252	1
c ₁	1	1
c_2	0.85252	0.91771
c_3	0	1
C ₄	3	. 1
c ₅	0	1
C_{lo}	0.5	0.75
C_{2o}	0.85252	1
V_e (eV)	-101.12679	-37.10024
V_{p} (eV)	20.69825	13.17125
T(eV)	34.31559	11.58941
$V_{m}(eV)$	-17.15779	- 5.79470
E(noiho)(eV)	0	-14.63489
ΔE_{H_2MO} (AOTHO) (eV)	0	-1.13379

$\begin{array}{cccccccccccccccccccccccccccccccccccc$			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	E_T (AOI HO) (eV)	0	-13.50110
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$E_T(H_2MO)(eV)$	-63.27075	-31.63539
$\begin{array}{c ccccc} \varpi\left(10^{15} \ rad \ / \ s\right) & 49.7272 & 26.4826 \\ \hline E_K \ (eV) & 32.73133 & 17.43132 \\ \hline \bar E_D \ (eV) & -0.35806 & -0.26130 \\ \hline \bar E_{Kvlb} \ (eV) & 0.19649 & 0.35532 \\ \hline E_{q.} \ (13.458) & Eq. \ (13.458) \\ \hline \bar E_{osc} \ (eV) & -0.25982 & -0.08364 \\ \hline E_{mag} \ (eV) & 0.14803 & 0.14803 \\ \hline E_T \ (Group) \ (eV) & -49.54347 & -32.28590 \\ \hline E_{initial} \ (AO/HO) \ (eV) & -14.63489 & -14.63489 \\ \hline E_{mitial} \ (AO/HO) \ (eV) & 0 & -13.59844 \\ \hline \end{array}$	E_T (atom – atom, msp ³ .AO) (eV)	-2.26759	-0.56690
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	E_r (MO) (eV)	-65.53833	-32.20226
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\omega \left(10^{15} rad / s\right)$	49.7272	26.4826
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	E_{κ} (eV)	32.73133	17.43132
E_{Kvib} (eV) [49] Eq. (13.458) \vec{E}_{osc} (eV) -0.25982 -0.08364 E_{mag} (eV) 0.14803 0.14803 E_T (Group) (eV) -49.54347 -32.28590 $E_{initial}$ (ϵ_i AO/HO) (eV) -14.63489 -14.63489 $E_{initial}$ (ϵ_i AO/HO) (eV) 0 -13.59844	\overline{E}_{D} (eV)	-0.35806	-0.26130
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	\overline{E}_{Kvib} (eV)	1	1
E_T (Group) (eV) -49.54347 -32.28590 $E_{initial}$ (ϵ_s AO/HO) (eV) -14.63489 -14.63489 $E_{initial}$ (ϵ_s AO/HO) (eV) 0 -13.59844	\overline{E}_{osc} (eV)	-0.25982	
$E_{initial}$ (ϵ_{A} AO/HO) (eV) -14.63489 -14.63489 $E_{initial}$ (ϵ_{S} AO/HO) (eV) 0 -13.59844	E_{mag} (eV)	0.14803	0.14803
$E_{initial}$ (s AO/HO) (eV) 0 -13.59844	$E_T(Group)(eV)$	-49.54347	-32.28590
		-14.63489	-14.63489
$E_D(Group)(eV)$ 5.63881 3.90454	$E_{initial}(s, AOIHO)(eV)$	0	-13.59844
	E_{D} (Group) (eV)	5.63881	3.90454

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. E_T is $E_T(atom-atom,msp^3.AO)$.

-								
Bond	Atom	\mathcal{E}_T	E_T	E_{τ}	E_{r}	Final Total	,	
		(eV)	(eV)	(eV)	(eV)	Energy) mai
		Bond 1	Bond 2	Bond 3	Bond 4	$C2sp^3$	(a)	(a_{\circ})
Ì						(eV)		
$\mid C - H (CH) \mid$	S	-0.85035	-0.85035	-0.56690	. 0	-153.88327	0.91771	0.79597
3-		20000						
C=HC=C	ン	-0.85035	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
a								

Bond	$\left \begin{array}{c} E_{\it Coulomb} \left(C2sp^3 \right) \! ({ m eV}) \end{array} \right \; \; \; \; \; \; \; \; \; \; \; \; \; \; \; \; \; \; $	$E(C2sp^3)$	ι,θ	θ	θ_2	d,	d,
	Final	(eV) Final	<u></u>	O	(O)	(a_o)	$\begin{pmatrix} a_0 \end{pmatrix}$
C-H(CH)	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C = HC_n = C$	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Relative Error	0.00006
Experimental Total Bond Energy (eV)	57.26340
Calculated Total Bond Energy (eV)	57.26008
СН	9
C = C	9
Name	Benzene
Formula	C,H,

Table 15.218. The bond angle parameters of benzene and experimental values [1]. E_T is $E_T(atom-atom,msp^3.AO)$.

2		
5	7	
C_2 C_1 C_2 Atom 2	0.79232 0.79232	
C ₂ Atom 1	0.79232	
Atom 2 Hybridization Designation (Table	34	
Ecaulombic Hy Atom 2 D	-17.17218	
Ecoulombic Atom 1 Atom 1 Designation (Table	34	
	2.62936 4.5585 -17.17218	
$2c'$ Terminal Atoms (a_0)	4.5585	
$2c'$ Bond 2 (a_0)	2.62936	
$2c'$ Bond 1 (a_0)	2.62936	
Atoms of Angle	2CCC (aromatic)	ACCH (aromatic)

The state of the s							
υ¨	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	E	φ,	0	θ,	Cal. θ	Exp. θ
		(eV)	(e)	· ©	_ 	<u></u>	٩
000/							
,-	0.70727	1 0501	-				120 150 531
ට	0.17636	-1.03030				120,19	120-00,021
HUU/	1						(penzene)
							120 (80 62)
aromatic)				120.19		119.91	[7C-0C] 07.1
			_				(henzene)

Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		Energy (eV)	Energy (eV)	
C₃H ₈	Propane	41.46896	41.434	-0.00085
C ₄ H ₁₀	Butane	53.62666	53.61	-0.00036
C ₅ H ₁₂	Pentane	65.78436	65.77	-0.00017
C ₆ H ₁₄	Hexane	<i>7</i> 7.94206	77.93	-0.00019
C ₇ H ₁₆	Heptane	90.09976	90.09	-0.00013
C ₈ H ₁₈	Octane	102.25746	102.25	-0.00006
C ₉ H ₂₀	Nonane	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126.57286	126.57	-0.00003
C11H24	Undecane	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	150.88826	150.88	-0.00008
C ₁₈ H ₃₈	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

•			•	
	*	Calculated	Experimental	Relative Erro
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C ₄ H ₁₀	Isobutane	53.69922	53.695	-0.00007
C ₅ H ₁₂	Isopentane	65.85692	65.843	-0.00021
C ₅ H ₁₂	Neopentane	65.86336	65.992	0.00195
C_6H_{14}	2-Methylpentane	78.01462	78.007	-0.00010
C ₆ H ₁₄	3-Methylpentane	78.01462	77.979	-0.00046
C ₆ H ₁₄	2,2-Dimethylbutane	78.02106	78.124	0.00132
C ₆ H ₁₄	2,3-Dimethylbutane	77.99581	78.043	0.00061
C ₇ H ₁₆	2-Methylhexane	90.17232	90.160	-0.00014
C ₇ H ₁₆	3-Methylhexane	90.17232	90.127	-0.00051
C ₇ H ₁₆	3-Ethylpentane	90.17232	90.108	-0.00072
C ₇ H ₁₆	2,2-Dimethylpentane	90.17876	90.276	0.00107
C ₇ H ₁₆	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C ₇ H ₁₆	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C ₇ H ₁₆	3,3-Dimethylpentane	90.17876	90.227	0.00054
C ₈ H ₁₈	2-Methylheptane	102.33002	102.322	-0.00008
C ₈ H ₁₈	3-Methylheptane	102.33002	102.293	-0.00036
C ₈ H ₁₈	4-Methylheptane	102.33002	102.286	-0.00043
C ₈ H ₁₈	3-Ethylhexane	102.30169	102.274	-0.00027
C ₈ H ₁₈	2,2-Dimethylhexane	102.33646	102.417	0.00079
C ₈ H ₁₈	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C ₈ H ₁₈	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C ₈ H ₁₈	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C ₈ H ₁₈	3,3-Dimethylhexane	102.33646	102.369	0.00032
C ₈ H ₁₈	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C ₈ H ₁₈	3-Ethyl-2-methylpentane	102.31121	102.277	-0.00033
C ₈ H ₁₈	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C ₈ H ₁₈	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C ₈ H ₁₈	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C ₈ H ₁₈	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C ₈ H ₁₈	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C ₈ H ₁₈	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C ₉ H ₂₀	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C ₉ H ₂₀	3,3-Diethylpentane	114.49416	114.455	-0.00034
C ₉ H ₂₀	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C ₉ H ₂₀	2,2,3,4-Tetramethylpentane	. 114.51960	114.492	-0.00070

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₉ H ₂₀	2,2,4,4-Tetramethylpentane	114.57316	114,541	-0.00028
C_9H_{20}	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126.680	0.00027
C ₁₀ H ₂₂	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₃ H ₆	Propene	35.56033	35.63207	0.00201
C ₄ H ₈	1-Butene	47.71803	47.78477	0.00201
C ₄ H ₈	trans-2-Butene	47.93116	47.90395	-0.00057
C ₄ H ₈	Isobutene	47.90314	47.96096	0.00121
C ₅ H ₁₀	1-Pentene	59.87573	59.95094	0.00121
C ₅ H ₁₀	trans-2-Pentene	60.08886	60.06287	-0.00043
C ₅ H ₁₀	2-Methyl-1-butene	60.06084	60.09707	0.00060
C ₅ H ₁₀	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C ₅ H ₁₀	3-Methyl-1-butene	59.97662	60.01727	0.00068
C ₆ H ₁₂	1-Hexene	72.03343	72.12954	0.00133
C ₆ H ₁₂	trans-2-Hexene	72.24656	72.23733	-0.00013
C ₆ H ₁₂	trans-3-Hexene	72.24656	72.24251	-0.00006
C ₆ H ₁₂	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C_6H_{12}	2-Methyl-2-pentene	72.37203	72.37206	0.00000
C ₆ H ₁₂	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C ₆ H ₁₂	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C ₆ H ₁₂	3-Methyl-trans-2-pentene	72.37203	72.33268	-0.00054
C ₆ H ₁₂	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C_6H_{12}	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C ₆ H ₁₂	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C ₆ H ₁₂	3,3-Dimethyl-1-butene	72.31796	72.30366	-0.00020
C_6H_{12}	2,3-Dimethyl-2-butene	72.49750	72,38450	-0.00156
C ₇ H ₁₄	1-Heptene	84.19113	84.27084	0.00095
C ₇ H ₁₄	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C ₇ H ₁₄	trans-3-Methyl-3-hexene	84.52973	84.42112	-0.00129
C ₇ H ₁₄	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C ₇ H ₁₄	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C ₇ H ₁₄	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C ₇ H ₁₄	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C ₇ H ₁₄	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C7H14	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C ₈ H ₁₆	1-Octene	96.34883	96.41421	0.00068
C ₈ H ₁₆	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C_8H_{16}	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C_8H_{16}	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C ₈ H ₁₆	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00055

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Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₃ H ₄ C ₄ H ₆ C ₄ H ₆	Propyne 1-Butyne	29.42932 41.58702	29.40432 41.55495	-0.00085 -0.00077
C ₉ H ₁₆	2-Butyne 1-Nonyne	41.72765 102.37552	41.75705 102.35367	0.00070 -0.00021

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF ₄ CHF ₃ CH ₂ F ₂	Tetrafluoromethane Trifluoromethane Difluoromethane	21.07992 19.28398 18.22209	21.016 19.362 18.280	-0.00303 0.00405 0.00314
C₃H₁F C₃H₁F	1-Fluoropropane 2-Fluoropropane	41.86745 41.96834	41.885 41.963	0.00314 0.00041 -0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

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Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl ₄	Tetrachloromethane	13.43181	13.448	0.00123
CHCl₃	Trichloromethane	14.49146	14.523	0.00217
CH_2Cl_2	Dichloromethane	15.37248	15.450	0.00217
CH₃Ci	Chloromethane	16.26302	16.312	0.00299
C_2H_5Cl	Chloroethane	28.61064	28.571	-0.00233
C₃H ₇ Cl	1-Chloropropane	40.76834	40.723	-0.00138
C ₃ H ₇ Cl	2-Chloropropane	40.86923	40.858	-0.00112
·C ₄ H ₉ Cl	1-Chlorobutane	52.92604	52.903	-0.00028
C_4H_9Cl	2-Chlorobutane	53.02693	52.972	-0.00104
C ₄ H ₉ Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00104
C ₄ H ₉ Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00037
C ₅ H ₁₁ Cl	1-Chloropentane	65.08374	65.061	-0.00037
C ₅ H ₁₁ Cl	1-Chloro-3-methylbutane	65.15630	65.111	
C ₅ H ₁₁ Cl	2-Chloro-2-methylbutane	65.36827	65.344	-0.00069
C ₅ H ₁₁ Cl	2-Chloro-3-methylbutane	65.16582		-0.00037
C ₆ H ₁₃ Cl	2-Chlorohexane	77.34233	65.167	0.00002
C ₈ H ₁₇ Cl	1-Chlorooctane	101.55684	77.313	-0.00038
C ₁₂ H ₂₅ Cl	1-Chlorododecane		101.564	0.00007
C ₁₈ H ₃₇ Cl	1-Chlorooctadecane	150.18764	150.202	0.00009
-1031	- CSTOOTHUCCHIC	223.13384	223.175	0.00018

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Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	_Energy (eV)	
CBr ₄	Tetrabromomethane	11.25929	11.196	-0.00566
СНВг₃	Tribromomethane	12.87698	12.919	0.00323
CH₃Br	Bromomethane	15.67551	15.732	0.00360
C ₂ H ₅ Br	Bromoethane	28.03939	27.953	-0.00308
C ₃ H ₇ Br	1-Bromopropane	40.19709	40.160	-0.00093
C₃H₁Br	2-Bromopropane	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	63.48143	63,477	-0.00007
C ₆ H ₁₃ Br	1-Bromohexane	76.67019	76.634	-0.00047
C7H15Br	1-Bromoheptane	88.82789	88.783	-0.00051
C ₈ H ₁₇ Br	1-Bromooctane	100.98559	100.952	-0.00033
C ₁₂ H ₂₅ Br	1-Bromododecane	149.61639	149,573	-0.00029
C ₁₆ H ₃₃ Br	1-Bromohexadecane	198,24719	198.192	-0.00029

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CHl₃	Triiodomethane	10.35888	10.405	0.00444
CH ₂ I ₂	Diiodomethane	12.94614	12.921	-0.00195
CH₃I	Iodomethane	15.20294	15.163	-0.00263
C ₂ H ₅ I	Iodoethane	27,36064	27.343	-0.00066
C ₃ H ₇ I	1-Iodopropane	39.51834	39.516	-0.00006
C ₃ H ₇ I	2-Iodopropane	39.61923	39.623	0.00009
C ₄ H ₉ I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₃ Cl	Chloroethene	22.46700	22.505	0.00170
C ₃ H ₅ Cl	2-Chloropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₄ O	Methanol	21.11038	21.131	0.00097
C ₂ H ₆ O	Ethanol -	33.40563	33.428	0.00097
C₃H ₈ O	1-Propanol	45.56333	45.584	0.00046
C₃H ₈ O	2-Propanol	45,72088	45.766	0.00098
C ₄ H ₁₀ O	1-Butanol	57.72103	57.736	0.00026
$C_4H_{10}O$	2-Butanol	57.87858	57.922	0.00020
$C_4H_{10}O$	2-Methyl-1-propananol	57,79359	57.828	0.00074
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048
C ₅ H ₁₂ O	1-Pentanol	69.87873	69 887	0.00048

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
$C_5H_{12}O$	2-Pentanol	70.03628	70.057	0.00029
$C_5H_{12}O$	3-Pentanol	70.03628	70.097	0.00087
$C_5H_{12}O$	2-Methyl-1-butananol	69.95129	69.957	0.00008
$C_5H_{12}O$	3-Methyl-1-butananol	69.95129	69.950	-0.00002
$C_5H_{12}O$	2-Methyl-2-butananol	70.31129	70.246	-0.00092
$C_5H_{12}O$	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	I-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
$C_7H_{16}O$	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
$C_9H_{20}O$	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
C ₁₆ H ₃₄ O	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	0.00174 -0.00030 -0.00086 0.00000 0.00075 -0.00059 0.00026 -0.00085 0.00081 -0.00055
		Energy (eV)	Energy (eV)	
C ₂ H ₆ O	Dimethyl ether	32.84496	32.902	0.00174
C_3H_8O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	81.86464	81.817	-0.00059
$C_6H_{14}O$	Disopropyl ether	82.06642	82.088	
$C_6H_{14}O$	t-Butyl ethyl ether	82.10276	82.033	-0.00085
C ₂ H ₁₆ O	t-Butyl isopropyl ether	94.36135	94.438	0.00081
$C_8H_{18}O$	Dibutyl ether	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	106.38182	106.410	
$C_8H_{18}O$	Di-t-butyl ether	106.36022	106.425	
$C_8H_{18}O$	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental	Relative Еггог
Lomaia	. Indilie		Total Bond	
		Energy (eV)	Energy (eV)	
CH₅N	Methylamine	23.88297	23.857	-0.00110
C₂H ₇ N	Ethylamine	36.04067	36.062	0.00060
C₃H ₉ N	Propylamine	48.19837	48.243	0.00092
C ₄ H ₁₁ N	Butylamine	60.35607	60,415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60,547	0.00148
$C_4H_{11}N$	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₇ N	Dimethylamine	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	60.22930	60.211	-0.00030
$C_6H_{15}N$	Dipropylamine	84.54470	84.558	0.00016
$C_6H_{15}N$	Diisopropylamine	84.74648	84.846	0.00117
C ₈ H ₁₉ N	Dibutylamine	108.86010	108.872	0.00011
C ₈ H ₁₉ N	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₃ H ₉ N	Trimethylamine	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	84.30648	84.316	0.00012
C ₉ H ₂₁ N	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₂ O	Formaldehyde	15.64628	15.655	0.00056
C₂H₄O	Acetaldehyde	28.18711	28.198	0.00039
C₃H ₆ O	Propanal	40.34481	40.345	0.00000
C ₄ H ₈ O	Butanal	52.50251	52.491	-0.00022
C_4H_8O	Isobutanal	52.60340	52.604	0.00001
C₅H ₁₀ O	Pentanal	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	101.13331	101.179	0.00045
C ₈ H ₁₆ O	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C ₃ H ₆ O	Acetone	40.68472	40.672	-0.00031
C_4H_8O	2-Butanone	52.84242	52.84	-0.00005
$C_5H_{10}O$	2-Pentanone	65.00012	64.997	-0.00005
C ₅ H ₁₀ O	3-Pentanone	65.00012	64.997	-0.00005
C ₅ H ₁₀ O	3-Methyl-2-butanone	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	<i>77</i> .15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
$C_7H_{14}O$	3-Heptanone	89.31552	89.287	-0.00032
$C_7H_{14}O$	4-Heptanone	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₇ H ₁₄ O	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
C ₈ H ₁₆ O	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
C ₉ H ₁₈ O	2-Nonanone	113.63092	113.632	0.00001
C ₉ H ₁₈ O	5-Nonanone	113.63092	113.675	0.00039
C ₉ H ₁₈ O	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH_2O_2	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
$C_3H_6O_2$	Propanoic acid	. 45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

			•	
		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	,
		Energy (eV)	Energy (eV)	
$C_2H_4O_2$	Methyl formate	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	142.51009	142,523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	57.76366	57.746	-0.00030
C₄H ₈ O ₂	Ethyl acetate	57.63888	57.548	-0.00157
$C_5H_{10}O_2$	Isopropyl acetate	69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate	69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate	81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate	82.23881	82.197	-0.00051

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087
$C_7H_{14}O_2$	Ethyl pentanoate	94.11198	94.033	-0.00084
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	106.44313	106.363	-0.00075
$C_8H_{16}O_2$	Propyl pentanoate	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	106.37057	106.384	0.00013
$C_9H_{18}O_2$	Butyl pentanoate	118.42738	118.489	0.00052
$C_9H_{18}O_2$	sec-Butyl pentanoate	118.52827	118.624	0.00081
$C_9H_{18}O_2$	Isobutyl pentanoate	118.49994	118.576	0.00064

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
, orman	·	Energy (eV)	Energy (eV)	•
CH ₃ NO	Formamide	23.68712	23.697	0.00041
C ₂ H ₅ NO	Acetamide	36.15222	36.103	-0.00135
C ₃ H ₇ NO	Propanamide	48.30992	48.264	-0.00094
C ₄ H ₉ NO	Butanamide	60.46762	60.449	-0.00030
C ₄ H ₉ NO	2-Methylpropanamide	60.51509	60.455	-0.00099
C ₅ H ₁₁ NO	Pentanamide	72.62532	72.481	-0.00200
C ₅ H ₁₁ NO	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
C ₆ H ₁₃ NO	Hexanamide	84.78302	84.780	-0.00004
C ₈ H ₁₇ NO	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₃ H ₇ NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C ₄ H ₉ NO	N,N-Dimethylacetamide	59.91404	59.890	-0.00041
C ₆ H ₁₃ NO	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	,
		Energy (eV)	Energy (eV)	
CH ₄ N ₂ O	Urea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₃ ClO	Acetyl chloride	28.02174	27.990	-0.00115

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Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_6O_3$	Acetic anhydride	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₃ N	Acetonitrile	25.72060	25.77	0.00174
C ₃ H ₅ N	Propanenitrile ·	37.87830	37.94	0.00171
C ₄ H ₇ N	Butanenitrile	50.03600	50.08	0.00082
C ₄ H ₇ N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C ₅ H ₉ N	Pentanenitrile	62.19370	62.26	0.00111
C ₅ H ₉ N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	86.50910	86.59	0.00089
C ₈ H ₁₅ N	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

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		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H ₂ S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH₄S	Methanethiol	19.60264	19.575	-0.00141
C ₂ H ₆ S	Ethanethiol	31.76034	31.762	0.00005
C ₃ H ₈ S	1-Propanethiol	43.91804	43.933	0.00035
C₃H ₈ S	2-Propanethiol	44.01893	44.020	0.00003
C₄H ₁₀ S	1-Butanethiol	56.07574	56.089	0.00024
C ₄ H ₁₀ S	2-Butanethiol	56.17663	56.181	0.00009
C ₄ H ₁₀ S	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
C ₄ H ₁₀ S	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
C ₅ H ₁₂ S	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
C ₅ H ₁₂ S	1-Pentanethiol	68.23344	68.264	0.00044
C ₅ H ₁₂ S	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
C ₅ H ₁₂ S	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
C ₅ H ₁₂ S	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
$C_6H_{14}S$	1-Hexanethiol	80.39114	80.416	0.00031
$C_6H_{14}S$	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
C ₆ H ₁₄ S	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	92.54884	92.570	0.00023
C ₁₀ H ₂₂ S	1-Decanethiol	129.02194	129.048	0.00020

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Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
		Energy (eV)	Energy (eV)	
C₂H ₆ S	Dimethyl sulfide	31.65668	31.672	0.00048
C₃H ₈ S	Ethyl methyl sulfide	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	55.97208	56.043	0.00076
$C_4H_{10}S$	Methyl propyl sulfide	55,97208	56.029	0.00120
$C_4H_{10}S$	Isopropyl methyl sulfide	56.07297	56.115	0.00102
$C_5H_{12}S$	Butyl methyl sulfide	68.12978	68.185	0.00073
C₅H ₁₂ S	t-Butyl methyl sulfide	68,28245	68.381	0.00081
$C_5H_{12}S$	Ethyl propyl sulfide	68.12978	68.210	0.00144
C ₅ H ₁₂ S	Ethyl isopropyl sulfide	68.23067	68.350	0.00117
$C_6H_{14}S$	Diisopropyl sulfide	80.48926	80.542	0.00174
$C_6H_{14}S$	Butyl ethyl sulfide	80.28748	80.395	0.00063
$C_6H_{14}S$	Methyl pentyl sulfide	80.28748	80.332	0.00133
C ₈ H ₁₈ S	Dibutyl sulfide	104.60288	104.701	
$C_8H_{18}S$	Di-sec-butyl sulfide	104.80466	104.701	0.00094
$C_8H_{18}S$	Di-t-butyl sulfide	104.90822	104.701	-0.00099
$C_8H_{18}S$	Diisobutyl sulfide	104.74800	104.834	0.00011
$C_{10}H_{22}S$	Ethyl propyl sulfide	128.91828		0.00082
$C_{10}H_{22}S$	Diisopentyl sulfide	129.06340	128.979	0.00047
		129.00340	129.151	0.00068

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₆ S ₂ C ₄ H ₁₀ S ₂	Dimethyl disulfide Diethyl disulfide	34.48127	34.413	-0.00199
$C_6H_{14}S_2$	Dipropyl disulfide	58.79667 83.11207	58.873 83.169	0.00129 0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond	Relative Error
C ₂ H ₆ SO C ₄ H ₁₀ SO	Dimethyl sulfoxide Diethyl sulfoxide	35.52450 59.83990	Energy (eV) 35.435 59.891	-0.00253 0.00085
C ₆ H ₁₄ SO	Dipropyl sulfoxide	84.15530	84.294	0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_2$	Dimethyl sulfone	40.27588	40.316	0.00100

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Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6SO_3$	Dimethyl sulfite	43.95058	44.042	0.00207
$C_4H_{10}SO_3$	Diethyl sulfite	68.54939	68.648	0.00143
$C_8H_{18}SO_3$	Dibutyl sulfite	117.18019	117.191	0.00009

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₂ H ₆ SO ₄	Dimethyl sulfate	48.70617	48.734	0.00058
C ₄ H ₁₀ SO ₄	Diethyl sulfate	73.30077	73.346	0.00038
C ₆ H ₁₄ SO ₄	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

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Formula	Name	Calculated	Experimental	Relative Error
1 Official	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH ₃ NO ₂	Nitromethane	25.14934	25.107	-0.00168
C ₂ H ₅ NO ₂	Nitroethane	37,30704	37.292	-0.00108
C ₃ H ₇ NO ₂	1-Nitropropane	49.46474	49.451	
C ₃ H ₇ NO ₂	2-Nitropropane	49.56563		-0.00028
C ₄ H ₆ NO ₂	1-Nitrobutane		49.602	0.00074
		61.62244	61.601	-0.00036
C ₄ H ₉ NO ₂	2-Nitroisobutane	61.90697	: 61.945	0.00061
C ₅ H ₁₁ NO ₂	1-Nitropentane	73.78014	73.759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
CHAIC		Energy (eV)	Energy (eV)	
CH ₃ NO ₂	Methyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH_3NO_3 $C_2H_5NO_3$ $C_3H_7NO_3$	Methyl nitrate Ethyl nitrate Propyl nitrate	28.18536 40.34306 52.50076	28.117 40.396 52.550	-0.00244 0.00131 0.00093
$C_3H_7NO_3$	Isopropyl nitrate	52.60165	52.725	0.00233

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Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C ₅ H ₈	Cyclopentene	54.83565	54.86117	0.00047
C ₄ H ₆	1,3 Butadiene	42.09159	42.12705	0.00047
C ₅ H ₈	1,3 Pentadiene	54.40776	54.42484	0.00084
C ₅ H ₈	1,4 Pentadiene	54.03745	54.11806	0.00031
C ₅ H ₆	1,3 Cyclopentadiene	49.27432	49.30294	0.00149

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated	Experimental	Relative Error
		Total Bond	Total Bond	
O TY		Energy (eV)	Energy (eV)	
C ₆ H ₆	Benzene	57.26008	57.26340	0.00006
C ₆ H ₅ Cl	Chlorobenzene	56.55263	56.581	0.00051
C ₆ H ₄ Cl ₂	m-dichlorobenzene	55.84518	55.852	0.00012
C ₆ H ₃ Cl ₃	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
C ₆ H ₃ Cl ₃	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C ₆ Cl ₆	Hexachlorobenzene	52.57130	. 52.477	-0.00179
C ₆ H ₅ NO ₂	Nitrobenzene	65.18754	65.217	0.00046
C ₇ H ₈	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
C ₇ H ₅ ClO ₂	2-chlorobenzoic acid	73.06193	73.082	0.00027
C7H5ClO2	3-chlorobenzoic acid	73.26820	73.261	-0.00010
C ₇ H ₅ ClO ₂	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C ₆ H ₇ N	Aniline	64.43373	64.374	-0.00023
C ₇ H ₉ N	2-methylaniline	76.62345	76.643	-0.00025
C ₇ H ₉ N	3-methylaniline	76.62345	76.661	0.00023
C ₇ H ₉ N	4-methylaniline	76.62345	76.654	0.00030
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72.47476	72.476	-0.00003
C ₇ H ₇ NO ₂	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
C ₇ H ₇ NO ₂	Aniline-3-carboxylic acid	80.90857	80.813	-0.00041
C ₇ H ₇ NO ₂	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C ₆ H ₆ O	Phenol	61.75817	61.704	-0.00087
C ₆ H ₄ N ₂ O ₅	2,4-dinitrophenol	77.61308	77.642	
C ₆ H ₈ O	Anisole	73.39006	73.355	0.00037
$C_{10}H_{8}$	Naphthalene	90.74658	90.79143	-0.00047
C ₄ H ₅ N	Pyrrole	44.81090	44.785	0.00049
C ₄ H ₄ O	Furan	41.67782	44.763	-0.00057
C₄H₄S	Thiophene	40.42501		0.00033
C ₃ H ₄ N ₂	Imidazole	39.76343	40.430	0.00013
C ₅ H ₅ N	Pyridine	51.91802	39.74106	-0.00056
C ₄ H ₄ N ₂	Pyrimidine	46.57597	51.87927	-0.00075
C ₄ H ₄ N ₂	Pyrazine	46.57597	46.51794	-0.00125
C ₉ H ₇ N	Quinoline	85.40453	46.51380	0.00095
C ₉ H ₇ N	Isoquinoline		85.48607	0.00178
C ₈ H ₇ N	Indole	85.40453	85.44358	0.00046
C ₅ H ₅ N ₅	Adenine	78.52215 70.83735	78.514 70.79811	-0.00010 - 0.00055

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Section V1

Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

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In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a 5 novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of 10 atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one 15 embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate 20 thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties.

- 5 Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input
- 10 means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or
- 15 special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which
- 20 cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include,
- 25 for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions,
30 molecular radicals, functional groups thereof, and related structure and property information
and produce useful data output and application of the parameters of these species, wherein the
nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills'
Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand
Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

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Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at http://www.blacklightpower.com/bookdownload.shtml, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl, C=C, C=O, CH3). Functional groups typically dictate or define properties and structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing

25 information about the structure, energies and names of molecules and functional groups: rawdata format and hierarchical format. In a raw-data file, all information is stored as is, below
the header describing the type of information. As shown in the Table below, for example, the
names of the molecule or functional group are listed below the #NAMES header. The names
and positions of the atoms are listed below the #ATOMS header, and so on.

```
#NAMES
       CH3
       Alkane CH3
       #SMILES
 5
       C-
      #ATOMS
             C
                          0
                                 0
      2
             Η
                    1.9775 -0.698 0
      3
             Η
                    -0.9888
                                 -0.698 1.712
      4
             H
                    -0.9888
                                 -0.698 -1.712
10
      #AO
                   0.171 2
       1
             1 1s
      2
             1 2sp3 0.864 -1
      #BONDS
      1
             12
                   1
                          1.649
      2
             13
                   1
                          1.649
      3
15
             14
                   1
                          1.649
      #BONDAXES
                   1
                          90
                                 0
                                       0
      #DATA
      RCH bond angle: 109.44°
      CH bond length: 2.097 a
20
      HFORM: 12.492
```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule.

30 Under the #GROUP_LINKS header is information about how these functional groups are connected to each other to construct pentane.

5

10

				517	<u></u>	
#NA	MES					
Pent	ane					
HON A	or pe					
	ILES					
CCC	CCC					
#GR	OUPS					
1	C-					
2	-C-				•	
3	-C-					
4	-C-					
5	-C- -C- C-					
#GR	OUP L	INKS				
1	1 Ī	21	180			
2 3	22	3 1	180			
3	3 2	4 1	180			
4	42	5 1	180			

Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule date file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

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first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'.

5 This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules, 10 provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CONTINUOUS-CHAIN ALKANES ($C_n H_{2n+2}$, $n = 3,4,5...\infty$)

The continuous-chain alkanes, $C_n H_{2n+2}$, are the homologous series comprising terminal methyl groups at each end of the chain with n-2 methylene (CH_2) groups in between:

$$CH_3(CH_2)_{n-2}CH_3$$
 (15.109)

- 5 C_nH_{2n+2} can be solved using the same principles as those used to solve ethane and ethylene wherein the 2s and 2p shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and
- energy. Three H AOs combine with three carbon $2sp^3$ HOs and two H AOs combine with two carbon $2sp^3$ HOs to form each methyl and methylene group, respectively, where each bond comprises a H_2 -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The CH_3 and CH_2 groups bond by forming H_2 -type MOs between the remaining $C2sp^3$ HOs on the carbons such that each carbon forms four bonds involving its four $C2sp^3$ HOs. For the alkyl C-C group, $E_T(atom-atom, msp^3.AO)$ is
- 15 $-1.85836 \, eV$ where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4,

- 20 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when c_2' is given as the ratio of two values of
- 25 c_2 designated to Atom 1 and Atom 2 and corresponding to $E_{Coulombic}$ of Atom 1 and Atom 2,

respectively, then
$$c_2' = \frac{c_2(Atom\ 2)}{c_2(Atom\ 1)}$$
.

Parameter	netrical bond param ('-(' Group	Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental value. Parameter $C = C$ $C = H (CH_3)$ $C = H (CH_3)$	alkanes and experi $C - H (CH_1)$	nental valu
a (u,)	2,12499	Group 1.64920	Group 1.67122	-
$c'(a_{\scriptscriptstyle \bullet})$	1,45744	1.04856	1.05553	
Bond Length 2c' (A)	1.54280	1.10974	1.1713	
Exp. Bond Length (A)	1.532 (propane) 1.531	1.107 (C - H propane) 1.117	1.107 (C-H propane) 1.117	•
h,c (a,)	1.54616	1.27295	1.29569	
u	0 68600	083580	02150	

Table 15.5. The MO to HO intercept geometrical bond parameters of straight-chain alkanes. E_r is $E_r(alinn-alian,msp^3AO)$. Bond R

			2	23.69	56.41	-16.49325	-16.68412	0.81549	17716.0	-153,47406	0	۰	-0.92018	-0.92918	3	11.50
	0,38106	1.83879	30.08	116.18	63.82	-15.56407	-15,75493	0.86359	0,91771	-152.54487	9	,		2,000		HC -CHCH
	0.29933	1.35486	35.84	25	Š	2000					,		•	-092918	ن	H.CC.H.CH.
			10.25		68.67	16 40124	-16.68412	0.81549	17710	-153.47406	•	•	-0.92918	-0.92918	C	$c = u \left(c u_1 \right)$
_	0.18768	1,23564	41.48	102.51	77.49	-15.56407	-15,75493	0.86359	0.91771	-152.54487	0	0	,	01/2/20		(11) 11
_													·	0.00019	,	('-H (CH.)
	(a°)	(°)	E	□	=	Final	Final	(° ₀)	()		Bond 4	Bond 3	Bond 2	Pond		
	, d ₄	d,	6 ° 3	6 ⁻ S	. e	<u></u>	((((((((((((((((((((o,)	Energy	(e ^y ,	(e)	(§)	(eV)		
						-	* -			Final Total	.,	Ŀ	22	:4	Atom	Bond

Table 15.6. The energy parameter			
Parameters	C – C Group	CH ₃	CH ₂
	<u> </u>	Group	Group
n _i	1	3	2
<i>n</i> ₂	0	2	1
<i>n</i> ₃	0	0	0
C_{ι}	0.5	0.75	0.75
C_2	1	1	1
c_{l}	1	1	1
c_2	0.91771	0.91771	0.91771
<i>c</i> ₃	0	0	1
<i>c</i> ₄	2	1	1
<i>c</i> _s	0	3	2
C_{1o}	0.5	0.75	0.75
C ₂₀	1	1	. 1
$V_{_{e}}(eV)$	-28.79214	-107.32728	-70.41425
V_{p} (eV)	9.33352	38.92728	25.78002
T(eV)	6.77464	32.53914	21.06675
$V_{m}(eV)$	-3.38732	-16.26957	-10.53337
E(AOIHO) (eV)	-15.56407	-15.56407	-15.56407
ΔE_{H_2MO} (AOTHO) (eV)	0	0	0
$E_{T}(AOIHO)$ (eV)	-15.56407	-15.56407	-15.56407
$E_{T}(H,MO)$ (eV)	-31.63537	-67.69451	-49.66493
$E_{\tau}(atom-atom,msp^3.AO)$ (eV)	-1.85836	0	0
$E_{\tau}(MO)$ (eV)	-33.49373	-67.69450	-49.66493
$\omega \left(10^{15} \ rad / s\right)$	9.43699	24.9286	24.2751
E_{κ} (eV)	6.21159	16.40846	15.97831
$\overline{\widetilde{E}}_{D}$ (eV)	-0.16515	-0.25352	-0.25017
\vec{E}_{Kvih} (eV)	0.12312 [2]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))
\overline{E}_{oxc} (eV)	-0.10359	-0.22757	-0.14502
E_{mag} (eV)	0.14803	0.14803	0.14803
$E_{T}(Group) (eV)$	-33.59732	-67.92207	-49.80996
$E_{initial}(c_{\downarrow}$ AOIHU) (eV)	-14.63489	-14.63489	-14.63489
$E_{initial}(c_s AOIHO) (eV)$	0	-13.59844	-13.59844
$E_{D}(Group)$ (eV)	4.32754	12.49186	7.83016

ACINICINA VALUES [J].														
I able 13.1. The total taking electrons of il-arkanes valuation and proposition and the energies of the capetinished and the earliest 31.	•													
	Relative	Епог		-0.00085	-0.00036	-0.00017	-0.00019	-0.00013	-0.00006	-0.00012	-0.00003	0.00004	-0.00008	0.00008
ייים ווסוויוצטלוווטט לי	Experimental	Total Bond	Energy (eV)	41.434	53.61	65.77	77.93	60:06	102.25	114.40	126.57	138.736	150.88	223.85
and the interiorial grot	Calculated	Total Bond Energy	(eV)	41.46896	53.62666	65.78436	77.94206	90.09976	102.25746	114,41516	126.57286	138.73056	150.88826	223.83446
יםו החושורת ה	CH.	•		-	7	"	4	٦,	9	7	∞	σ	2	9
II-GIRGIES	CH.	•	1	2	7	7	7	7	7	7	7	2	7	2
CICE STORY	2-3			7	m	4	s	9	7	œ	6	2	=	81
י זור וחומו חחות	Name			Propane	Butane	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Undecane	Dodecane	Octadecane
ו מחום	Formula	•		ř. Ľ.	ÇH.º	C3H12	Ç,H;•	C,H,s	CH,	SH SH SH	CloHz	C,H3	$C_{11}H_{24}$	C _{IR} H ₃

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of θ , the parameters from the preceding angle were used.

							_
<u>.</u>	Ехр. <i>θ</i>	107 (propanc)	112 (propune) 113.8 (butane)	111,0 (butane)			
dem.m	(s)	108.44	110.49	110,49	109.50	109.44	100 44
יי – מנס	(e)						
Cr. (010	(e)						
ร น้ำ	, (°)		69.51	15'69		70.56	70 64
iigie were usea.	E_{r} (eV)	0			0		
i eceuing a	وخ	1.15796			96251.1		
חווו חוב ל	Մ	0.75			0.75		
amerers m	5	ı			<u>.</u> .		
o,, uie pai	כי	1					
חומווסוו סז	C ₂ Atom 2.	1			-		
ווו וווב כמוני	C ₃ Atom I	0.86359			0.86359		
and captullicated values [1]. It the calculation of σ_c , the parameters much be confined angle were used. E_T is $E_T(aloin-aloin, mp$, $AO(c)$.	Atom 2 Hybridization Dosignation (Table 15.3.A)	×			π		
ווו באלבו וווו	Errulamed	н	,		Ξ		
	Atom I Hybridization Designation (Table 15.3.A)	7			7		
יווקטוופוסיי	Éroekunklı Attorn I	15.75493 C,			15.75493 C,		
amercia	2c' Terminal Atoms (a ₀)	3.4252			3.4252		
angıc ba	2c' Bond 2 (a _o)	2.1110			2,0971		
nile polie	2c' Bond I (a ₀)	2.11106			2.09711 2.0971 3.4252 15.73493 C.,		
Table 10.6. The bolld alighe parameters of sinarghi-chair	Atoms of Angle	Mathylana ZHC_H 2.11106 2.1110 3.4252 15.75493	בר"כ"כ ^י	H,2,22	Methy! ZHC, H	'2"2"27 ·	H J J/

BRANCHED ALKANES ($C_n H_{2n+2}$, $n = 3, 4, 5...\infty$)

The branched-chain alkanes, $C_n H_{2n+2}$, comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH₂), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene 5 functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ((CH_3) , CH) and t-butyl ((CH_3) , C) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those 10 used to solve the methyl and methylene functional groups wherein the 2s and 2p AOs of each C hybridize to form a single 2sp3 shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_r(atom-atom, msp^3.AO)$ of each C-C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.85836 \, eV$ or $-1.44915 \, eV$ based on 15 the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918 \, eV$ (Eq. (14.513), or methyl, $-0.72457 \, eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. 20 (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each E_D (corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

Constituted Constitute	G G i
Functional Group	Group Symbol .
CH₃ group	$C-H(CH_3)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

0,38106 0.45117 0,51388

1.K3K79 1.90890 1.97162 0.50570

0.18708 0.18708 0.27726

1.35486 1.35486

°0 °c

(°, a

Ī	_					_			7	-	_
	(C)	Group	2.10725	1,45164	1.53635	1,532	(propane)	1.531	(butane)	1,52750	0.68888
	(e) CC	Group	2.10725	1,45164	1.53635	1.532	(propane)	1.53[(butano)	1.52750	0.68888
	(g)	Graup	2.12499	1,45744	1.54280	1.532	(bropane)	1.531	(butane)	1.54616	0.68600
	(<u>G</u>)	Group	2,10725	1,45164	1.53635	1,532.	(propane)	1.531	(butane)	1.52750	0.68888
	(a)	Croup	2.12499	1,45744	1.54280	1.532	(propane)	1.531	(butane)	1.54616	0 68600
The state of the s	(e) (J)	Огостр	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1,54616	0 68600
LICE DINGINGS DING ON	H~.)	Groin	1.67465	1.05661	1,11827		1.122	(isobutane)		1.29924	0 63005
Materials of Orani	(H.J) H - J	Oronn	1,67122	1.05553	1,11713	1,107	ĩ		(C - H butane)	1.29569	051570
able 13.10. The requirement will parameters of district around by the capacitics and capacitics.	(7.7) 777	Ground Caronia	1.64920	1.04856	1,10974	1.107	(C-H propane)	1111	(C - H butane)	1,27295	002574
1 apre 13.10.	Parameter		0 (0,1)	c. (o")	Bond Length 2c' (A)	100	LAp. 50mg	100	<u> </u>	h,c (a,)	

Table 15.11. The MO to HO intercept geome	etrical bond	netrical band parameters of branched-cliain alkanes. R,R',R" are H or alkyl groups. E_r is E_r (atum – atom, aisp',A(2)	ranched-chain al	kanes. R.R.R'	are Horalkyl	groups. Er is	Er atum - at	om.nisp'.AO).					
Волд	Atom	1,7	E,	E,	£,	Final Total	,	5	£(c'240')	$E(C2sp^3)$.0	θ,	φ"
		(e)	(eV)	(eV)	(s _V)	Energy	(°	(a,	(e)	્રે	©	©	©
		Bond 1	Bond 2	Bond 3	Bond 4	(58g)		(-8)	Final	Final			
('-H (CH,)	ن	41,9291K		0	e	-152.54487	12216,0	0.KG359	-15.75493	-15,56407	77.40	102.51	8b.11.
C-H (CH ₃)	ن	*1162617	AL929FR	°	c	-153.47406	0,91771	0.81549	-1468412	-16,49325	68.47	111.53	33.84
C - H (CH)	ij	41 9291R	-419291K	-0.92918	c	+2£0+751-	17716,0	0,77247	-17.61330	-17,42344	61.10	118.90	11.37
H,C,C,H,CH,	ن	XIGZO'U*	c	c	0	-1:52.54.H7	17719,0	0.86359	-15,75403	-15,56407	63.82	116,13	30.08
H,C,C,H,CH, ~	ئ: "	41,020,1k	4(929)X	8	e e	-153,47406	17716.0	0.81549	-10.68432	-16.49325	56,41	123.59	36.05
$R + H_1C_{\bullet}C_{\bullet}(H_1C_{\bullet} - R)HCH_1 - CC_{\bullet}C_{\bullet}(B)$	ئ	41,929 lk	41,92,918	41.9291R	æ	154.40324	17710,0	14£77.0	-17.61330	-17,42244	48.30	131.70	21.90
$n - H_1^{C}(R^{-} + H_1^{C})C_1(R^{-} + H_1^{C})CH_1 - CC_1(C)$	ť	WI929IX	78,457,04	-0.72457	251721'0"	-154.71860	17710,0	ด.75หพ	-17.92866	677571-	48.21	131.79	21.74
$i\omega C_s C_s (H_1 C_s - R)HCH_1 - C_s C_s (d)$	ن	40,92918	K1020.05	\$10 <u>2</u> 0,0-	D.	-154,4034	17716.0	0.17247	-17.61330	P\$22F'L -	48.30	131.70	21.90
$(enC_*(R'-H_1C_*)C_*(R''-H_1C_*)(H_1-(C'-C'))$:	A.72457	15167.0-	-0.72457	-41,72457	-154.51399	17719.0	0.76765	-17.92866	-11.73779	50.04	129.96	2266
$IeH(_{\mathcal{L}}^{*}\mathcal{L}_{k}(H_{k}C_{r}-R)HCH_{k}-CC(C)$		40,72457	81626'0-	810 <u>2</u> 0.0-	.0	-154,19863	0.91771	0.78155	-17.40469	-17,21783	52.78	127.23	3,
$lsoC_{*}(R-H_{1}C_{s})C_{*}(R^{*}-H_{1}C_{s})CH_{s} - (C-C_{s}(0))$	ن:	-0.72457	-0,72457	-0.72437	40.72457	154,51399	0.91771	0.76765	-17.92866	-17,73779	\$0,04	129.96	35.66

Table 15.12. The energy parameters (eV) of functional groups of branched-chain alkanes.	ters (ev) of function	onal groups of bra	anched-chain alkan						
Parameters	CH,	CH_1	H-0	C-C (a)	(q) D-0	(e) C-C (e)	C-C (d)	(e) D-D	C-C(f)
	Group	Group	caroup	Croup	Ciroup	Group	Group	Group	Group
7,	3	2	-	ı	-	-	-	-	-
n_2	2	-	0	0	0	0	0	0	c
n,	0	0	0	0	0	0	0		
כ'	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	20
້ວ	1	-	-	-	-	-			
c ₁	1	-	_	1	-	-	_	_	
5	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	17710	0.91771	0.91771
·5	0	-	-	0	0	0	-	-	0
٠,	-	-	_	2	2	2	2	2	2
5	3	2	-	0	0	0	0	0	0
C _E	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
٠.٠	-	_	-	1	1	1	ı	I	-
V, (eV)	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (&V)	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
1 (67)	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(samo) (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{n_1 s m}(s n_1 m)$ (eV)	0	0	0	0	0	0	0	0	0
$E_r(.mim)$ (cV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-1535946	-15.35946
$E_r(n_s,m)$ (eV)	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom - atom, msp^3.AO)$ (eV)	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_{\uparrow}(\iota m)$ (eV)	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10's rad/s)	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_{κ} (eV)	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E_n (eV)	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{\rm kink}$ (eV)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
Em (eV)	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emery (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{r}(\iota_{iuur})$ (eV)	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Enter (c. will) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Einhind (c. : 101110) (eV)	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
En (inver) (CV)	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Formula	Formula Name		ulated using th	ne runcuonai	calculated using the initiational group composition and the energies of Table 15.12 compared to the experimental values [3]	on and the end	rgics of Table	15.12 compare	d to the experi	nental values [3].		
		,	ř.	3	C ~ C (a)	(e) ひーひ	(e)ひーひ	C-C (q)	C -C (c)	() 2-2		Experimental	Relative Erro
											Total Bond	Total Bond	
Z. H.	Isobutane	3	0	-		-		ļ			Energy (eV)	Energy (eV)	
Ç.	Isopentana		_		• •		> 0		0	0	53.69922	\$3,695	-0.00007
£.	Neopentane	- 4	. د	- c	- «	٠,	5	0	0	0	65.82692	65.843	1,0000
J. H.	2-Methylpentane		٦,	> -	۰ د	۰ د	4	0	0	0	65.86336	65 992	20100
S. F.	3-Methylpentane		٦.		7	-	0	0	0.	0	78 01462	78 007	01000
±	2.2-Dimethylburane	•	7 -		~	•	0	0	0	0	78 01462	070 77	2000
		•	_	0		0	₹	0	•		10,000	616.11	0.00046
<u>ت</u> روا	4.3-Dimelhylbutane	4	c	7	0	. 7	٠ .	> -	> 0	۰ د	78.02106	78.124	0.00132
ÇF	2-Methylhexane	17	•	-					5	0	77.99581	78.043	0,00061
Ω, H,	3-Methylhexane	•				٠,	> 0	٥.	0	0	90.1732	90.160	-0.00014
ŋĦ,	3-Ethylpentime	, ,,,			٠.	• •	>	0		0	90.17232	90.127	130000
C,H,K	2,2-Dimethylpentane	. 4	, ,	- <	-	~ 1	۰.	0	0	c	90,17232	20.108	-0 0000
C,H,	2,2,3-Trimethylbutane	• •	ı c	>	٦ <	> 1	~ /		0	c	90.17876	90.276	0.00107
ņ, H,	2,4-Dimethylpentane	. 4	. –	- •	> <	•	•	0	0		90,22301	90 262	0.00044
CH	3.3-Dimethylpentane	. 4	- ^	× •	> (φ.	0	0	0	0	90.24488	90 233	21000
C,H	2-Methylheorans	. ,-	٠.	> -	7	o 1	~	0	0	0	90.17876	90.227	0.0004
H	3-Methylheptane		• •	- .	d -	n	0	0	٥	0	102,33002	102 422	80000
H.C.	4-Methylheneane	יו ני	+ -		4	m	0	0	0	0	102 33002	102 203	20000
ä	2. Code (Il. const.)	٠.		-	4	m	0	ó	c		נטטבב כטו	100.00	0.000.0
# # #	2 Dimeterale	m .	4	_	m	7	0		• 0	•	2005.201	102.286	-0.00043
	tit-Cilicani liexane	4	_	0	m	c	4	_		• •	20102.00	107.74	.0.00027
Ē:	7,3-Dimethylbexane	4	7	7	7	. 7	٠ -		> 0		102.33646	102.417	0.00079
Į,	2,4-Dimethylhexane	₩.	7	7	-		• <	- «	> (0	102,31121	102,306	-0.00005
H.	2,5-Dimethylbexane	4	2	7		·	> <	> 0	-	0	102.40258	102.362	-0.00040
Ť	3,3-Dimethylliexane	4	. 647		- ~		۰ د	ъ,		0	102,40258	102.396	-0.00006
Ŧ.	3,4-Dinnethylliexane	4	. 7	, ,		> <	d c	ь.	0	0	102,33646	102,369	0.00032
Ŧ.	3-Ethyl-2-methylpentane	4	. ~		• •	, ,	> 0	- .	0	0	102.31121	102.296	-0.00015
Ŧ.	3-Ethyl-3-methylpentane	4	1 1-4	• =	4 (*	. c	> -		0	0	102.31121	102.277	-0.00033
Ŧ.	2,2,7-Trimethylpentane	3		• -	- د	> r	4 -	-	0	0	102,33646	102,317	-0.00019
H.	2,2,4-Trimethylpentane	~	_	-	- c		٠,	0 (0	_	102,38071	102,370	-0.00010
EH U	2,3,3-Trimethylpentane	2	_		s ~	٠.	.	.	0	0	102.40902	102.412	0.00003
C,H	2.3.4-Trimethylpentane	~			- د	. .	n (۰ د	>		102,38071	102,332	-0.00048
Ç,H,	2,2,3,3-Tetramethylbutane	. 9		, c	• •	n <	.	~ •	0	0	102.29240	102.342	0.00049
ÇH	2,3,5-Trimethylhexane	~			> <	> r	.	0	_	0	102.41632	102.433	0.00016
CH;	3,3-Diethylpentane	4	9	. <	> =	~ «	.	_	0	0	114,54147	114.551	0.00008
Ç.F.	2,2,3,3-Terramethyloentans			, ,	• -	۰ ،	.	0	o	0	114,49416	114.455	AF000 0-
C,H,3	2,2,3,4-Terramethylogitans			· r	- 6	۰ د	9	0	-	0	114.57402	114.494	-0 000 20
C,H,2	2,2,4,4-Terramethylpentane			۹ (> <	~ (m.	-	0	-	114,51960	114.492	-0.00024
S,H,C	2,3,3,4-Terrameliylpeniane			> ć	> <	۰ د	uc i	0	•	0	114.57316	114.541	-0.00028
ClaHu	2-Methylnonane		.	, -	> <	4 (7	٥	0	7	114.58266	114.484	-0.00086
Cir.H.	Methylangan	٠.			و	m	o	0	0	0	126 64542	126.680	0.0000
1000	- Including	-	9	_	·		•	•		,	10.04	120.000	0.00027

Table 15.13. The total hand energies of branched alkanes calculated using the functi

.

able 15.14.	l he bond	angle pa	rameters	ot branched-	lable 15,14. The bond angle parameters of branched-chain aikanes and	d experiment	and experimental values [1]. In the calculation of θ ,, the parameters from the preceding angle were used. E_T is $E_T(atom - atom, m \mu p' AO)$	he calculati	ion of θ , th	e paramete	rs from the	preceding:	g angle wer	reused. E_r is E	, atom	– atom, n	nsp'.AO	<u>.</u>	
Atoms of Anglo	2 <i>c'</i> Bend 1 (<i>a_q</i>)	2c' Bond 1 (a _n)	2c' Terminal Atoms (a,)	Erminenhir Alam I	Atom I Hybridization Designation (Table 15.3.A)	Ermboarkie Atom 2	Atom 2 Hybridization Designation (Table 15.3.A)	C ₂ Atean I	C, Alom 2	טֿ	S	u.	૪	<i>E</i> _r (eV)	ø, ©	(°)	6. ©	§ ° €	Exp. θ (°)
Methy forc	2.11106	211106	3.4252	-15.75493	7	=	н	0.86359	-	-	-	0.73	1.15796	0		-		108.44	107 (propane)
<i>בב"כ"כ</i> י														·	69.51			110.49	112 (propane) 113.8 (butane) 110.8 (isobutane)
т.'c''н			<u> </u>												69.51			110.49	111.0 (butane) 111.4 (isobutane)
Methyl ZHC, H	2,09711	2.09711	3.4252	-15.75493	7	н	æ	0.86359	-	-	-	0.75	1.15796	o				109.50	
2C,C,C,															70.56			109.44	
4,0,02															70.56	-		109.44	
"ວ ^{ເຊ} ່ວ ວັວ7	2.91547	2.91547	4.7958	-16.68412 C,	25	-16.68412 C.	. 25	0.81549	0.81549	-	_	-	0.81549	-1.85836				110,67	110.8 (isobutane)
10 C, H	2.91547	2,11323	4.1633	-15,55033 C,	v	-14.82575 C,	-	0.87495	17716.0	0.75		0.75	1.04887	6				110.76	
2C,C,H to C,	2.91547	2.09711	4.1633	-15.55033 C,	5	-14.82575 C,	-	0.87495	17716.0	0.75	-	0.75	1.04887	0			-	111.27	111.4 (isobutane)
حرد"د" ادار"د"	2.90327	2.90327	4.7958	-15.55033 C,	5	-14.82575 C.	I	0.87495	0.91771	0.73	-	0.75	1.04887	-1,85836				111.27	111.4 (isobutane)
7C,C,C,												-			72.50		ŀ	107.50	

ALKENES $(C_n H_{2n}, n = 3, 4, 5...\infty)$

The straight and branched-chain alkenes, $C_n H_{2n}$, comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: C vinyl single bond to -C(C) = C, C vinyl single bond to -C(H) = C, and C vinyl single bond to $-C(C) = CH_2$. In addition, CH_2 of the $-C = CH_2$ moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups (CH₃) at each end of the chain, and may comprise methylene (CH₂), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds 15 can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of 20 the 2s and 2p AOs of each C to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. $E_r(atom-atom, msp^3.AO)$ of the C=Cbond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759 \, eV$, given by Eq. (14.247). $E_r(atom-atom, msp^3.AO)$ of each 25 C-C-bond MO in Eq. (15.52) is $-1.85836 \, eV$ or $-1.44915 \, eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918 \, eV$ (Eq. (14.513), or methyl, $-0.72457 \, eV$ (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The 30 geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each $E_D(G_{PRIMP})$ of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage 5, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(G_{PRIMP})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

ents.	Oroup Symbol	CHC	(C)		(- (- (m))	$C-H$ $\{CH_1\}$ $\{0\}$	$C - H$ (CH_3)	Can Can July	(1) (1)	#-U	(a) (b) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	(a) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	(3) (3)	(a) (b) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	(e)	() - (i)
Table 15 15 The symbols of functional groups of alkenes.	Functional Group	CC double bond	C vinyl single bond to -C(C)=C	C vinyl single band to -C(H)=C	C vinyl single band to -C(C))-CH2	CH, alkenyl group	e ser HO		CH, alkyl group	Đ	CC bond (n-C)	CC bond (iso-C)	CC bond (tert-C)	CC (iso to lso-C)	CC (110 1-C)	CC (t to igo-C)

		_	_						_	т	_	
C-C (f) Group	2.10725	1 45164		1,53635		1 532	(propane)	(buttane)	1,52750		0.68888	
ر (و) رکار	2,10725	27137	2017	52925		5	(propane)	(butane)	1 5750	20.30	0.68888	
Group Group	2 12499		1.45/44	1 64290	1.342.00		(propure)	(butane)	1,54516	01076.1	0.68600	
C-C (c) Group	2,107.5	7017	1.43164	36363.	1,53633	1	(propane)	(butane)		06/25.1	0.68888	
C – C (b) Group	Ourci c	2.16497	1.45744		1.54280		(propane)	(buttane)		1.54616	0.68600	
C~C (a) Group	20,000	2.12499	1.45744		1.54280		1.532 (propane)	1.53 l (buttane)		1.54616	0.68600	
dnoub Group		1.67465	199501		1.11827		1.122	(isobutane)		1 29974	0.61005	COCCA
$C-H\left(CH_{s}\right)$	Group	1.67122	1 05553		1.11713	1 107	(C - H grocens)	1.117 (C-H	butane)	1 20560	100.62.1	0.03139
$C-H(CH_3)$ C		1.64920	1 07056	orom.	1.10974	1 107	(C - H	1,117	butane)	20000	66777'1	0.63580
C-H (CH,)		1.64010	,,,,,,,	1.04.366	1.10668		1.10	1.108 (avg.)			1.26354	0.63756
C-((ii) Group		2,04740		1.43087	1.51437			(2-methy (propene)			1,46439	0.69887
('-(' (ii)		2.04740		1,43087	1.51437			1.508 (3-butere)			1,46439	0.69887
parameters of alk		7 04740		1.43087	1 51417	1001					1.46439	0.69887
Table (5. (6. The geometrical band parameters of alkenes and experimental Parameter $C = C = C \cdot (i) \cdot C \cdot C \cdot (ii)$	<u></u>	8000	077/4	1,26661	1 2405	25045.1	1.342 (2-methylpropere)	1,346 (2-butere)	1.349	1 - Constitute	0.75055	01038
Table 15.16. The Parameter			(a) u	c' (a,)	Bond Length	2c, (v)	Fvo Rend			_	h.c (a,)	

Table 13.17. The MO to not intercept geometrical bond parameters of alker	netheal bon	d parameters of	ŭ	R_i is an alkyl group and R,R',R' are H or alkyl groups.	d R.R.R are	H or alkyl grov		E_r is $E_r(atom - atom, msp^3, AO)$	usp. 40).						
Bond	Atom	E. E.	, E	E	£,	Final Total	200	7	$\mathcal{E}_{a_{a_{a_{a_{a_{a_{a_{a_{a_{a_{a_{a_{a_$	$E(C2\eta^3)$	θ,	9	9	d,	ď
		Bond 1	Bond 2	Bond 3	(ev) Bond 4	C25p ²	(a)	(a)	(eV)	(eV) Final	€	€	٥	(a°)	(°)
$C_r(H)C_s = C_s(H)C_s$	ن:	-1.13380	-0.9291R	د	c	-153.67867	0.91771	0,80561	-16.88873	-16.69786	127.61	\$2.39	58.24	0.77493	0.42168
$C_{\bullet}(H)C_{\circ} = C_{\bullet}H_{\bullet}$	٠,	-1.13380	c	С	5	-152.74049	17716,0	0.85252	-15.95955	-15.76BGR	129.84	50.16	60.70	0.72040	0.54620
C_(C_)C_ = C_H.C_		-1.13380	-0.72457	-0.72457	c	-154,19863	177;6.0	0.78155	-17.40869	-17.21783	126.39	53,61	\$6.95	0.80289	0.46371
$RC_{i}H_{i} - C_{i}(C) = C$ $(C - C_{i}(i))$	Ċ,	-1.13380	-0.72457	-0.72457	c	-154.19863	17719.0	0.78155	-17.40869	-17,21783	60.88	119.12	27.79	1.81127	0.38039
$R_{G_{i}}^{c}H_{i}^{c}-G_{o}^{c}(G)=C$ (C-C,0) $R_{G_{i}}^{c}H_{i}^{c}-C_{i}(G)=(CH_{i}$ $\{C-C,(Gii)\}$	3	11,72457	-0.92918	·s	c	-153.26945	0.91771	D,825/22	16,47951	-16.2864	07'79	112.60	31.36	1,74821	0.31734
$R_{C,H_3} - C_s(H) = C$ $(C - C_s(ij))$	Ų.	-1,13380	40.92918	c	e	-153,67866	177100	0,80561	-16.83X73	-16 69786	64.57	115.43	29.79	1.77684	0.34596
$R(C,H_1-C,(H)=C)$ $(C-C,(0))$	C.	41.020.0-	H1026:0-	a ·	c	-153.47405	17710.0	Q.R.I 549	16 (841)	-16,49325	65.99	114,01	30.58	1.76270	0.33183
C-H (CH1) (I)	ij	-1.13380	в	U	c	-152.74949	ודדועס	0.85252	15,95955	-15.7686R	77.15	102.85	41.13	1.2351	0.18963
C - H (CH ₅)	ij	81 <i>626</i> ,0-	O	a	=	-152,54487	17710,0	0,86359	-15.75-193	-15.56407	77.49	102.51	41,4%	1,23564	0.14704
C = H (CH ₁) (ii)	ij	-0.929{H	N1020.0-	Б	U	-153 47406	17710,0	0.81549	-16,68412	-16,49325	68.47	111.53	35.84	1.33486	0,29933
C-H (CH)	ij	40,9291K	81626,0-	-0.92918	c	154 40324	17716.0	0.17247	-17.61330	-17.42344	61.10	118.50	31.37	1.42988	0.37326
$H_1C, C, H_2CH_1 - (C-C, (a))$	Ů,	410 <u>2</u> 0,0-	o	٥	c	-132.54487	17710.0	0,86359	-15.75493	-15.56407	63,82	116.18	30.08	1.138779	0.38104
H,C,C,H,CH, - (C, -C,(n))	c.	40.92918	*1626 0	¢	=	90727'551*	17716,0	0.81549	-16,68412	-16,49325	16.41	123.59	24,76	1.90800	0.45117
$R = H_1C_1C_1(H_1C_2 - R^2)HCH_1 = (C - C_1(b))$	ر:	81626'0"	81020.0	40.92918	c	154,4034	17710.0	0.77247	-17.61330	-17,4224	44.30	B.161	21,50	1.97162	0.51388
$R = H_1C_2(R^2 - H_2C_2)C_3(R^2 - H_3C_2)CH_2 - (C - C^2)C_3$	ڻ	-(1.9291k	41,72457	-0,72457	4,72457	-154,71860	17714.0	0.73889	-17.92KGG	-(1.73779	-18.21	131.79	21.72	1.95734	0.50570
$ton',C_*(H_1C_*-R)HCH_1-(C-C_*(d))$	ڻ	-1:9291K	-1.9291R	-0:9291K	0	154,47324	17716,0	0.77247	-17.61330	-17,42244	48,30	07.161	21.90	1.97162	0.51388
$(R_{i}, R_{i}, R_{i}, R_{i}) C_{i} (R^{*} - H_{i}C_{i}) C_{i} + C_{i} C_{i} = C_{i} C_{i}$	ڻ	-0.72457 .	40 72457	-0.72457	-0.72457	-154.51399	0,91771	0,76765	17.92×G6	917.67.71-	50.04	129.36	22.66	1.94462	0,49298
renC_C_(H;C_, -R')HCH, - (C - C'(f))	i, t	0.72457	*16261 >	xi6z6u-	ન	-154, 19863	17719.0	0.78155	-17,40869	-17,21783	32.78	12.721	24.04	1.92443	0.47279
(C-C'(f))	ڻ	-0.72457	18771.15	-11.72457	-0,72457	.154.51309	0,91771	0,74765	-17.92866	647.57.11.	50.04	120.96	22.66	1,94462	0.4020#

ale 15.17. The MO to HO intercept geometrical bond parameters of alkenes. It is an alkel cross and R. R. R. are H or alkel intercept geometrical bond parameters of alkenes.

Table 15.18. The energy parameters (eV) of functional groups of alkenes	rs (eV) of func	tional groups	of alkenes.										}	6
Parameters	C=C	C-C (i)	C-C (ii)	C-C (iii)	CH, (i)	CH,	CH, (ii)	C - H Group	C-C (a) Group	Group	(e) U-U	C-C (4)	Group	Group
"	2	-	-	-	22	3	2	-	-	-	-	1	-	-
		0	c	0	-	2	_	0	0	0	0	0	0	0
",	,	, c	, c	, c		0	0	0	0	0	0	0	0	0
٠, ١	0.0	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
77	0.91771	-	-	-	-	-	-	-	-	-	-	-	-	-
	_		_	-	-	-	-	-	-	-	-	-	-	-
1,	0.91771	0.91771	0.91771	0.91771	0.91771	17716.0 -	17716.0	17716.0	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771
2	0	_	0	-	-	0	-	-	0	0	0	-	-	0
, c	4	2	2	2	-	 -	-	-	2	2	2	2	2	2
7	0	0	0	0	2	3.	2	-	0	0	0	0	0	0
- 0	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
3	17716.0	-	-	-	_	-		-	_		-	-	_	1
7 (67)	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	21,48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	34.67062	7.37432	7.37432	7,37432	21.95990	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (8V)	-17.33531	-3.68716	-3.68716	-3.68716	-10.97995	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(round) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
DE (nound) (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Er (some) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{\mathbf{r}}(n,n)$ (eV)	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T(atom - atom, msp^3, AO)$ (eV)	-2.26759	-1.44915	-1.85836	-1.44915	0	0 .	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (m) (eV)	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-67.69450	49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
w (1013 rad/s)	43.0680	9.97851	16.4962	9.97851	25.2077	24.9286	154.2.751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
Er (eV)	28.34813	6.56803	10.85807	6.56803	16.59214	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
Ē, (eV)	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exist (eV)	0.17897	0.15895	0.09931	0.09931	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	0.12312	0.12312 [2]
E. (eV)	-0.25568	-0.08827	-0.16869	-0.11809	127720-0-	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emg (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (inut) (eV)	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emile, (r #1111) (aV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Element (e. willer) (eV)	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	٥	0	٥	٥	0
$E_{D}(i_{comp})$ (aV)	7,51014	3.75498	4,39264	3.78480	7.83968	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.19. The cotal band energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy E,, that is subtracted from the velighted sum of the E_o(o-v) (eV)

Formula	Formula Name C=C	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	.)- <u>.</u>)	زدن	ひーン	CH, (i)	C#3	CH, (ii)	#3	ن ان	υ <u>-</u> υ	<u>ن</u> -ر	-C	2-5	(a) コーコ	E)	Calculated	Experimental	Relative
			ε	Ξ	•		•			•	€	<u> </u>	9	<u> </u>			Total Bond Energy (eV)	Fotal Bond Energy (eV)	Error
Ι	Property	6	6	-		1	-	0	-	0	0	0	0	-	0	0	35.56033	35,63207	0.00201
1	Butene	. –				-			_	_	0	0	0	0	۰	٥	47.71803	47,78477	0.00140
	Tana-2-Butene	_			•	c	7	0	7	0	0	0	0	٥	٥	0	47.93116	47,90395	-0,00057
	I cohomo			C	2	-	2	٥	0	0	0	٥		0	0	0	47.90314	47.96096	0.00121
	Bacteria			-	· c	-	-		_	-	0	0	0	0	0	0	59.87573	59.95094	0.00125
	וינ פונופנום	- •		- •	•	- <	٠,		۰ ۲					c	۰ د		98880 09	60 06787	.0 00043
E H	irans-Z-l'entene	٠.	-	7 (۰ د	> -	4 (4 0			• <		• •	• •		60.06034	20700	09000
	2-Methyl-1-butene		۰ د	۰ د	7 (- (7 1	- 0	٠.	-		•	> <		• •	• •	55A(C 03	60.16/44	20000
	2-Methyl-2-butene	_	_	_	•		•	э,	- ,	5	۱ د	> (- 0	> 0	-	> 0	60,21433	00.1044	20000
	3-Methyl-1-butene		٥	-	0	-	"	0	7	0	7	۰ د		-	-	-	20076.66	77/10/00	0.0000
	1-Hexene	-	0	_	٥	-	-	m	-	m	0	0	0	0 1	0	٥,	72.03343	72.12954	0.00133
	trans-2-Hexene	_	0	7	0	0	7	2	7	7	0	0		0	0	0	72.24656	72.23733	-0.00013
	trans-3-Hexene	-	0	7	0	0	7	7	7	7	0	0	0	0	0	•	72,24656	72.24251	-0.00006
	2-Methyl-1-pentenc	_	0.	0	7	-	7	~	0	7	0	0	0	0	0	•	72,21854	72,29433	0.00105
	2-Methyl-2-mentons		,	_	0	0	•	_	_	_	0	0	0	0	0	٥	72,372,03	72,37206	0.0000
	2-Mathyl-1-pontene					_	^	_	2	_	7	۰	0	0	0	0	72,13432	72.19173	0,00080
	A Market I promise		• •		, c	. -	۰ ۰		۰,			c	c	•	o	0	72,10599	72 21038	0.00145
	delineter year content	•	•	-	•						,								
C. H.	J-Methyl-trans-2-	_	2		٥	>	~	-	-		0	0	0	0	0	0	72,37203	72,33268	-0.00054
_	pentene																		
, H.	4-Methyl-trans-2-	-	c	^	c	0	m	c	•		7	0	0	0	0	0	72.34745	77.31610	-0.00043
	pentene	•	•													,	1		
ï	2-Ethyl-1-butene	_	0	0	M	-	7	7	0	4	c	0	0	0	0	0	72.21854	72.25909	0,00056
Ŧ	2,3-DimethyH1-bulene	_	c	0	64	-	m	0	_	0	7	0	0	0	D	0	72.31943	77.32343	0.00008
£	3.3-Dimethyl-1-butene		0	-	0	-	m	c	_	0	٥	'n	0	0	0	7	2.31796	72.30366	+0.00020
£	2.3-Dimethyl-2-butene	-	4	٥	0	٥	4	c	0	0	0	0	0	0	0	0	72.49750	72,38450	-0.0015G
· -	1-Hentone	-	0	-	0		_	4	_	4	0	0		۰	0	0	84.19113	84.27084	0.00095
	5-Methyl-1-hexene	_	0	_	0		7	7	2	_	m	۰	0	0		c	84.26369	84,30608	0.00050
1 2	trans-3-Methyl-3-hexene	-	7	_	0	0	rn	7	_	7	•	0	c	0	0	0	84.52973	84.42112	-0.00129
	7 4-Dimethyla samtene	-	c	•	2	-	m	-	_	0	•	c	0	0	0	0	84.44880	84,49367	0.0005
	4 4-Dimethyl-1-protene	-	c		. 0	_	, ra	_	_	0	0	4	0	0	0	0	84.27012	84,47087	0.00238
	2 4-Dirnethyl-2-nentene	_	. ~	-	0		•	0	~ ~	0	7	0	0	0	0	0	84.63062	84.54445	-0.00102
	remed 4-Dimerhod-2-		1			0				,	•	,	•	,	•	,	***************************************	9	70000
CHE	nentene	-	0	7	0		4		2	٥	0		ò	9	د	?	8454016	かんないま	0.0000
	2.Februla Lametholds					_				,	,	,	•	•	•			41077	
. TH'S	butene	-	0	0	7			-		-	7	0	0	>	>	5	C1//4/2	01744.68	0,000
	2.3.3-Trimethyl-1-		•	•	•	-	•	,	•		•	·	•	•	c	,	724.5.49	01110	2000
THE	buteno	-	•	>	~		e	>	5	>	>	• •	>	>	>	7	t/215:48	67117:40	200
H.U	1-Octens	-	0	0	-	-	-	~	_	s	•	0	Ö	0	0	0	96.34883	96.41421	0.00068
_	trans-2,2-Dimethyl-3-	-	<	r	•	٥	-	-	,	-	-	~	0	c	c	c	96.69846	96 68787	-0 000 1
ž	hexens	-	,	•	>		,	-	4	•	•	,	•	•	•	•			
7	3-Ediyl-2-methyl-1-	-		c	•	_	,-	,	_	,	,	c	c	c	٥	0	96.63483	96.61113	-0.0002
9	pentene		•	,	•		1		•		•	,	,	•	,				
7.	2,4,4-Trimethyl-1-	_	0	0	7	-	4	_	0		ь	4	•	0	0	0	96.61293	96.71684	0.00107
1	pentene				,														
CHH,	2,4,4-Truncthyl-2-	0	7	-	•	5	.	0	-	0	0	m	٥	0	0	ņ	96.67590	96.65880	-0.00018
:	pentene	,	•		•	-		٠		•	•		•	•	c	•	20175 061	07635 061	27000
ή. Ε.	1-Decene	- -	0 0		- c			۰ د		- 0	> c	> Ø	> c	> c	> <	> c	144 97963	145.07163	0.00003
2 E :	I-Dodecene		•		> <	;-		\ :		N <u>C</u>	> <	١ <	۰ د	, ,	,	ه د	103 61043	77.17.501	0000
	- Heverane	-	=	_	=		-	-	-	7	2	>	>	3	>	>	720,000		,,,,,,

	Εχρ. <i>θ</i>			13.44 (1.3.5.heartiene CbCcCe) 13.17 (1.3.5.heartiene CbCcCe) 13.44 (1.3.busaiene CCC) 12.44 (1.3.busaiene CCC) 12.5		118.5 (2-methylpropene)	121 (2-methytpropene)	107 (prepane)	12 (propans) 113.8 (butane) 10.8 (Fenbutane)	(butane) (butane) 111.4 (isobutane)				110.8 (isobutane)		111.4 (stobutane)	111,4 (Sabutane)	
	Cal. <i>9</i> (°)	118.36	113.84	123.46	118.19	1631	121.85	108.44	110.49	110.49	109.50	109.44	109,44	110.67	110.76	111.27	111.27	107.50
	θ _t (°)				13.46													
	(°)				11836		(16.31											
	(°)								69.51	15'69		70.56	70,56					72.50
is $E_r(atom - atom, nsp^3, AO)$.	Ε _τ (eV)	0	-1.85836	-1.85836			,	c			0			-1,85836	o	0	-1,85836	
(atom = ato	<i>و</i> ',	1.07647	0.81549	0.81055		1.17300		1.15796			1.15796			0.81549	1.04887	1.04887	1,04887	
Er is Er	ራ	0.75	1			0.75		0.75			0.75			-	0.75	0.75	0.75	
	ပ်	-	,	- .		-		1			1				-		1	
ding angle	ن ن	0.75		-		-		-						-	0.75	0.75	0.75	
n the prece	C ₂	0.91771	0,81549	0.81549		-		-			-			0.81549	17710.0	0.91771	17719.0	
meters fro	C ₂ Attent 1	0.85252	0.81549	0,80561		0.85252		0.86359			0.86359			0,81549	0.87495	0.87495	0,87495	
tion of 8,, the par	Atom 2 Hybridization Designation (Table 13.3.A)	-	24.	77		æ		H			н			. 25	-	1	1	
n the calcula	E'colombie Atom 2	-14.82575 C,	-16.58411 C.	-16.68411 C.,		H		н			#			-16.68412	-14 62573 C.	-14.82575 (',	-14.83575 (',	
ental values [1].	Atom I Hybridization Designation (Table 15.3.A)	6	24			۰	,	7			7			25	•	\$	\$	
and experim	Erminate Aim I	15.95954	-16.63411 C,	-1688873 C,		-15.95955		-15,75493			-15.75493			-16.68412 (',	-15,55033 C_	-15,55033	15.55033	
alkenes	2c' Torniasi Alivin (a ₀)	4,2895	4.7958	4,7539		3,4756		3,4252			3.4252			4.7958	4,1633	4,1633	4.79SB	
meters of	2c' lb-13 (a,)	2.86175	2.86175	2.86175		3.04578		2,11106			2.09711			2.91547	נגנווג	1.09711	2,90327	
d angle para	2c' Read i (a ₀)	211323	2 86175	125322		2.04578		2.11106			2.09711			2.91547	2.91547	2.91547	2.90327	
Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of 0,, the parameters from the preceding angle were used.	Alims of Angle	ZHC,C, $(C,(H)C,=C,)$	(c,(c,)c, = c,) ∠c,c,c,	(c'=c'c') 7c'c'c'	,2,7HZ	$\angle HC_{\mu}H$ $\left(H_{1}C_{\mu}=C_{1}C_{\mu}\right)$	(H,C, = C,C,)	Mathickers ZHC, H	לנ"נ"נ".	H"5"37	Methy! ZHC",H	70,00	H*,5,22	سي ر.* حر. ار "ر."	ייי נ" קנ:"נ."H קני	ZC,C,H in C,	ומן נ" קנ"נ" נ"	".J".J".

ALKYNES
$$(C_n H_{2n-2}, n = 3,4,5...\infty)$$

The straight and branched-chain alkynes, C_nH_{2n-2} , have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound C, these C-C-bond MOs are defined as primary and secondary C-C functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal CH of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p

20 AOs of each C to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp³ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. E_T (atom – atom, msp³.AO) of the C ≡ C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of acetylene, –3.13026 eV, given by Eq. (14.342). E_T (atom – atom, msp³.AO) of each -alkyl-bond MO in

25 Eq. (15.52) is –1.85836 eV or –1.44915 eV based on the energy match between the C2sp³ HOs corresponding to the energy contributions equivalent to those of methylene, –0.92918 eV (Eq. (14.513), or methyl, –0.72457 eV (Eq. (14.151)), groups, respectively. For the C-C groups each, comprising a C single bond to C ≡ C, E_T (atom – atom, msp³.AO) is –0.72457 eV based on the energy match between the C2sp³ HOs for the mutually bound C of the single and triple bonds. The parameter ω of each group is matched for oscillation in the transition state based on the group being primary or secondary.

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The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each C of the $C \equiv C$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

C triple band to $C = C$ (1) C single band to $C = C$ (2°) C single band to $C = C$ (2°) C single band to $C = C$ (2°) CH (terminal) CH, group CH, group CH, group CH (alkyl) CC band (ter-C) CC band (ter-C) CC band (ter-C) CC (to to C) CC (to to C) CC (to to C)	Table 15.21. The symbols of functional groups of alkynes.	alkynes.
and to C = C (!*) and to C = C (!*) at) c.) c.) se-C.) se-C.)	Functional Group	
nd to C g ((*) al) (c) (c) (c) (r) (r) (r) (r) (r	CC triple bond	
ad to C ≈ C (2°) al) c) c) co so-C) so-C) c) c)	C single band to C & C (19))
(b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	C single band to C = C (2°)	S ()
()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es ()-es	CH (terminal)	(1) H)
	CH, group	C-H (CH.)
	CH ₂ youp	(HJ)H-J
	CH (alkyl)	(1)
	CC bond (n-C)	(1) (1)
	CC bond (iso-C)	3 3 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
	CC bond (ten-C)	(0) ; - ;
	CC (iso to iso-C)	(S) (1) (1)
	CC (t to 1-C)	
	CC (r to iso-C)	(3)

Table 15 27 T	Table 15 27 The meaning land anomalian of the	in the second se			ı	,							
Parameter) = J	())-)	(:-('(ii)	-('(ii) C-H(i)	C-H (CH.)	(H.J) H-J	- 1	(6) (7-1)	(H) (J = ()				
	Group	Group	Group	Group	Group	Crucia C	Group	Group	Gmap	Oroup	Croup	(a) (b) (c) (c) (d)	
0 (%)	1.28714	1.99185	1.99185	1.48719	.1.64920	1.67122	1.67465	2 12499	2 17480	1000			danis
$\langle c, (a_s) \rangle$	1.13452	1.41133	1,41133	0.99572	1.04856	1.06663	1 0666 1		7,10,21	4.10723	2.12499	2,10725	2.10725
Bond Length						200000	Igoco'i	1.45/44	1.45744	1,45164	1.45744	1.45164	1,45164
2c' (A)	1.20072	1.49369	1.49369	1.05383	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1 53635	36963 1
	200				1 107	1 107							Contract of
Exp. Bond	(acetylene)				H-2)	H-0)		1.532	1.537	153			
	1,208	1,450 (2,4-hexadiyna)	1,450 (2,4-hexadiyne)	1.060 (acetylene)	propane)	propane)	1.122	(propane)	(propane)	(propane)	(propane)	(propane)	(propane)
					#-0)	(C-H	(sonnane)	(butane)	(53) (hidane)	1.531	1.83.	1.531	1.531
					butane)	butane)		()	(Distance)	(outsuc)	(ontane)	(Dutane)	(butane)
n.c (a,)	0.60793	1.40557	1.40557	1.10466	1.27295	1.20569	1 29924	SARIE	2000				
23	0.88143	0.70835	0.70866	230770	00000		10//07/	010461	1.34010	06/26.1	1.54616	1.52750	1.52750
			2000										

Bond	Atom	E.	. F.	E,	ω	Final Total	Ţ	Í	E. (C2r)	E(C2xp)	.0	9	6	ď	ď,
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy (2xp²	(a _b)	(a°)	(eV) Final	(ev) Final	©	E	· ©	(e)	(a)
NC,C,C, -H	ن.	-1,5/513	c	c	٥	-153,1MMZ	17710.0	0.83008	-16,39088	-16.20001	26.92	10.08	48.71	0.98144	0.01428
C,C,=C,H	·	-1.56513	-0.36229	۰	0	1153.54311	17710,0	0.81213	-16.7317	-16,56231	137.17	42.83	65.25	0.53820	0.59562
C,C, m C,H	٠٠	-1,54513	•	c	c	-153,18082	17710,0	0.83008	-16.30088	-16.20002	187.91	42.09	66.24	0.51853	0.61599
C, -C, =C,H	٠٠	40,36220	-0.9291B	•	•	-152,90716	17710,0	0.84418	-16,11722	-15,92636	15.27	10,29	15.39	1.61974	0.20341
C - H (CH ₃)	ť	R1020.0-	c	c	۵.	-152.54487	177160	0.86359	-15.75403	-15.56407	77,49	16251	41,48	1.23564	0.18708
C-H (CH ₃)	U	41.92518	8102C/D-		•	-153,47406	17116,0	0.81549	-16,68412	-16,49325	68.47	111.53	35.84	1,35486	0.29933
C-H (CH)	ن	40,9291X	*I626.0-	A19291X	0	-154.40324	17716.0	0.77247	-17.61330	-17.42244	61.10	118,90	31.37	1.42,988	0,37326
H,C,C,H,CH, - (C - C. (a))	ij,	#10Z6'0	c	c	0	-152,54487	17116.0	0,16359	-15.75403	-15,56407	29'09	116.18	30.08	1.83879	90186.0
H,C,C,H,CH, (C -C, (a))	.5	#1626'0*	н1626'а-	=	Đ	153.47406	17716.0	0.11549	-16.68412	-16 49325	36,41	123.59	2606	1,90890	0,45117
$n - H_1C_sC_s(H_1C_s - R)HCH_1 - (C - C_1b)$	ئ	A.9291X	RIGZG'O*	% [GZG '0"	c .	-154,40324	14416.0	0 77247	17.61330	-17.42244	48.30	02.161	21.90	1.97162	0.51388
$R - H_1C_2(R' - H_1C_2)C_3(R'' - H_1C_2)CH_3 - (C - C'(c))$	ئ	#16ZG'0-	-0.72457	-0.724\$7	-0.72MS7	02817,461.	17716.0	0,75889	-17.92866	611.11.	48.21	62'161.	21.74	P5734	0.50570
$lsoC_sC_s(H_1C_s - R^s)HCH_1 - (C - C^s(d))$	ຜ	xt6ZG'U	0.U2018	#1626'0	a	-154,40324	17716.0	0.77247	17,61330	-17.42244	48.30	07.161	21.90	1,97162	0.51388
$ler(C_s(R^n - H_sC_s)C_s(R^n - H_sC_s)CH_s - (C - C_s(e))$	ڻ	-0.72457	-0.72457	15F21'0-	0.72457	-154.51399	17716.0	0,76765	-17.92866	617.571-	50.04	129.96	9977	Cyrrs'i	0.49298
$ler(C,C,(H_1C,-R^1)HCH_1-(C-C,(f))$	C.	T2457.0-	*1626'0-	\$16ZG'0-	ą.	-154,19863	1,11,6,0	0.78155	-17,408.69	-17.21783	\$2.78	22,751	24.04	1,92443	0.47279
$L(C-C, (R)) = H_1(L_2)C_4(R'-H_1(L_2)C'H_1 - C')$	2	41,72457	-0.72457	-0.72457	0.72457	-15451399	17716.0	0,76765	17.92866	-17,73779	¥0'0\$ ·	129.96	22.66	1,94462	0.49298

Dammeters			,										
· manifolds	ひ m ひ Group	(i) Croup	Group	Group	Group,	CH,	Group	C~C (a) Group	(a) (b) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	C-C (e) Groun	C-C (d)	(e) C – C	C-C(f) Group
$n_{\rm i}$	3	_	_	-	3	2	-	-		丄	-	-	-
n_{2}	0	0	0	0	2	-	c	-	٠			- -	- -
n,	0	c	6	0				,	, ,	, (,	,	، ا
C	5	, ,	, ,	27.0	, ,	2			2	>	3	0	٥
			3	67.5	57.50	5	0.0	0.5	0.5	0.5	0.5	0.5	0.5
5	_	-	-	-	-	-	-	1		_	_	1	1
ان	_	-		-	-	-	-	_	_	_	_		
c ₁	0.91771	0.91771	0.91771	0.91771	17716.0	17716.0	0.91771	17716.0	17716.0	0.91771	17716.0	0.91771	17716.0
رئ	2	-	-	0	0	-	_	0	o	٥	-	_	0
c,	٥	2	2	-	-	-		2	2	2	2	2	2
5	0	0	c	-	3	7	ı	0	0	0	0	0	0
C,,,	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C <u>.</u>	-	_	-	1	-	-	_	-	-	_	-	-	-
V, (eV)	-182.53826	-31.29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
7 (eV)	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (eV)	-35.45438	- Į	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3,45250	-3.45250
E(wino) (eV)	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{\mu_1 \mu \sigma}(.r_{nm})$ (eV)	0	-0.72457	-0.72457	-3.130269	0	0	0	٥	0	0	c	0	0
$E_r(\omega_{mo})$ (eV)	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_T(H,LO)$ (eV)	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31,63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3.AO)$ (eV)	-3.13026	-0.72457	-0.72457	0	0	0	o	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_r(sn)$ (eV)	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33 08452	-33 08452
w (1013 rad / s)	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9 55643
$E_{\rm K}$ (eV)	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	6.21159	621159	10.19220	621159	6 29021	6 29021
E_{o} (eV)	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24%6	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{k,\omega}$ (gV)	0.27773 [9]	0.08989	0.08989 [9]	0.35532 Eq	0.35532 Eq.	0.35532 Eq.	0.35532 Eq.	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
E (cV)	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0.14502	-0 07200	-0.10359	907570	700510	0 10160	9010	9001
Eng (aV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0 14803
$E_{T}(\omega_{mr})$ (eV)	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33 18712	-33 18712
Eneral (c. villo) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Eneral (c. MOTIN) (eV)	0	٥	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{D}(i_{busp})$ (eV)	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.24. The energy parameters (eV) of functional groups of alkynes.

	Relative Error		-0.00085	-0.00077	0,00070	-0.00021
	Experimental		29,40432	41,55495	41.75705	102.33367
	Calculated Total Bond Fourse	(eV)	29.42932	41.58702	41.72765	26676301
	C-C (C)		•	0 0		
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Pormula Name CEC (['		g	2 1		211	Table 16 36 The hand and
amma			- Buryne			15 36 TL
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Table 15.26. The h	and angle n	ametere	of alkyne	7							,	3	•	•	102.37552		102.35367	-0.00021
Numeral August 22. $2c^2 - 2c^2 - 2c$	26'	3,7	alkynt	s and exper	imental values [1].	In the calcul	ation of θ , the par	rameters fro	om the prece	ding angle v	vere used.	E, is E,	atom - aton	$n, msp^3 AO$).				
	(a ₀)	(a,)	Tenninal About (a ₀)	Climbandir Alaqui I	±" E	Cratenate Ann 3	Nom 4 Hybridization Designation	C3 Alem I	C ₁	ڻ-	ر ځ	ئ	ъ	E, (eV)	(e) (e) (e)	(C)	Og. (c)	Exp. 8 (9)
(C,C, a C,A)							C.C.									_	9	
Methy has ZHC, H	2.11106	2.11106	3,4252	-15.75493	7	H	=	0.86359	-	-	-	873	1.15796		-	-		107
		_		L									+	Ì		_	108.44	(propane)
72'.'.'7				·							·· ,		·····		69.51		110.49	(propane) (propane) (propane)
												1	+					(isobutane)
H'O'O															15.69		110.49	0,111.0 (Dutane)
ZHC, H	2.00711	2.09711	3.4252	-15.75493	-	=	1	0 86340	-	1.	-				+	1		(isobume)
70,07									-	-	-	6.73	1.15796	•			109.50	
4C,C,H	L									1		1			20.56		109.44	
70,0,0	291547	2.91547	4.7958	-16.68412	22	-16.68412	,	0000				1			70.56		109.44	
ZC.C.H				1.000		٠,٠	:	6.010.0	0.01349	-	-	-	0.81549	-1.85836			110.67	110.8 (isobutane)
ji (,	2.91547	2,11323	4.1633		~	-14.82575 C.		0.87495.	0.91771	0.75	_	0.75	1.04887	0			71.076	
4C,C,H	2.91547	2.00711	4 1633	-15.55033		-14,82575		1	į			+	+		-	\downarrow		
7007			\int			-		CENTO'S		90	-	0.75	1.04887	•			111.27	111.4 (fsobutine)
len C.	2,90327	2.90327	4.7958	-13,330 <u>4</u> 3	•	-14.12573 C,	-	0.87495	17716.0	0.75		27.0	1,04887	-1.85836	-	_	11 12	111.4
7C,C,C,								1			1		1	·				(isobutane)

ALKYL FLUORIDES
$$(C_n H_{2n+2-m} F_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$$

The branched-chain alkyl fluorides, $C_n H_{2n+2-m} F_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by a fluorine. The C-F bond comprises a functional group for each case of F replacing a H of methane in the series $H_{4-m}C-F_m$, m=1,2,3,4, and F replacing a H of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-F functional groups comprises the hybridization of the 2s and 2p AQs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the F AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the F AO has an energy of $E(F) = -17.42282 \, eV$. To meet the equipotential condition of the union of the C-F H_2 -20 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the

$$c_2\left(C2sp^3HO \text{ to } F\right) = \frac{E\left(C, 2sp^3\right)}{E(F)}c_2\left(C2sp^3HO\right) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}}(0.91771) = 0.77087 \quad (15.110)$$

C-F-bond MO given by Eqs. (15.68) and (15.70) is

 $E_T(atom-atom, msp^3.AO)$ of the C-F-bond MO in Eq. (15.52) based on the charge donation from F to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the F atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^5$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane, E_{mag} is positive since the term due to the fluorine atoms cancels that of the CH group. The C-C bonds to the CHF group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CF group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Table 13.27. The symbols of	i functional groups of branched
Functional Group	Group Symbol
CF of $CF_m H_{4-m}$	C-F (i)
CF of $C_n H_{2n+2-m} F_m$	C-F (ii)
CH ₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H$ (CH_2)
СН	C – H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	<i>C−C</i> (e)
CC (t to iso-C)	C-C (f)

- 	('-H ((:H,)) Group 1,64920 1,04836 1,10974 1,107 (C-H propare (.C-H burne) 1,27205	(C – H (CH,) Group 1,64920 1,04836 1,10974 (C – H butane) (C – H butane) 1,27295
	-5)	Group 1,31202 1,31202 1,31838 1,3838 (G-(methyl fluoride) (C-

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Table 15.29.		
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	Group	Group	Group	Group	Croup		Cronb	dies	5	Grade	dioin	dnoun	1	dnon		
0 (0")	1.72139	1,72139	1.64920	1,67122	1.67465	_	2.12499	2,12499	2.10	2.10725	2,12499	2.10725	-	2.10725		
c. (a)	1.31202	1,31202	1.04856	1.05553	1.05661	199	1.45744	1,45744	1.45	1.45164	1.45744	1.45164	_	1.45164		
Bond Length 2c' (A)	1.38858	1.38858	1.10974		1.11827	827	1.54280	1.54280	1.53	1.53635	1.54280	1.53635		1.53635		
Exp. Bond Length (A)	1.382 (methyf fluoride)	1.382 (methyl fluoride)	1.107 (C - H propane) 1.117 (C - H butane)	1.107 (C - H propane) 1.117 (C - H balane)	(isobutane)		1,532 (propane) 1,531 (butane)	1.532 (propane) 1.531 (butane)	(prop. 1.5 1.5	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)		1.532 (propane) 1.531 (butane)		
h,c (a,)	1,11435	1.11435	1,27295	-	1.29924	-	1.54616	1.54616	1.52	1.52750	1.54616	1.52750		1.52750		
l v	0.76219	0.76219	0.63580	0.63159	0.63095	H	0.68600	0.68600	0.68888	888	0.68600	0.68888		0.68888		
Table 15.29.	Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides. R,R',R" are	cept geometrical by	and parameters of b	ranched-chain alkyi	i fluorides. R.	Ξ	or alkyl groups.		E_r is $E_r(a_{lom}-a_{lom,mxp},\mathcal{A}O)$.(OF						
Bond		Atom	1 1	-	123	1	Final Total		13	Eradon	E(C2sg2)	.6	8	9	ď	6
· ······ ········				(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy (:2xp² (eV)	(%)	(a)	(cV) Final	(eV) Finai	(.)	(o)	(e)	(a,)	(a,)
$H_{L_{\bullet}}C_{\mu}^{*}-F_{\mu}^{*}$ (C, -F (i))		ن' —	-1,34946	0	•	0	-152.96515	0.91771	0,84115	-16.17521	-15,98435	100.77	19.13	47.86	1,15488	0.15714
$H_{+-}C_{-}-F_{\bullet}$ ((C _* - F (i))			-1,34946	0		0		0.78069	0.84115	-16,17521		100.77	22.57	47.16	1,15488	0.15714
-H ₂ C,C,F (C, -F (ii))		ບໍ	-1,34946	-0.92918	0	0	-153.89433	0,91771	0,79546	-17,10440	16.91353	97.02	82.98	45.11	1,21483	0.09718
-H ₂ C,C,F (C, -F (ii))		t t	-1 34946	0	0	a		0.78069	0.84115	-16,17521		1001	19.23	47.86	1.15488	0.15714
C-H (CH,)		i.	-0.92918	c	•	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1.23564	0.18708
C-H (CH)		ن -	-0.92918	-0.9291\$	0	0	-153,47406	17716.0	0,81549	-16,68412	-16.49325	68.47	111.53	35.84	1.35486	0.29933
C-H(CH)		U	40,92918	-0.92918	0.92918	0	-154,40324	17716.0	0.77247	-17,61330	-17,42244	61.30	118.90	31.37	1,4291	0.37326
$H_1C_*C_*H_1CH_1-(C-C_*(a))$	4, -	υ ,	-0,92918	•	0	0	-152.54487	0.91771	0,16359	-13.75493	-13.56407	28.69	116.18	30.08	1.83879	0.38106
(C-C (a))	4,-	ປ	-0.92918	-0.92918	٥.	o	-153,47406	0.91771	0.81549	-16,68412	-16.49325	36.41	123.59	26.06	1.90890	0.45117
$R = H_{\mathcal{L}, \mathcal{L}, \mathcal{L}}$	$R = H_2C_{s,s}(H_2C_{s} - R^{s})HCH_3 - (C - C_{s,s}(b))$	ບໍ	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.17247	-17.61330	-17,42344	48.30	131.70	21,90	1,97162	0.51388
(C-(c))	$R = H_2C_{*}(R' - H_2C_{*})C_{*}(R' - H_2C_{*})CH_2$.;) <i>cu</i> :- C	-0.92918	-0.72457	-0.72457	.0.72457	-154.71860	0.91771	0.75889	-17,92866	-17.7779	48.21	131.79	21.74	1.95734	0.50570
(C-C (d))	$IsnC_{i,C_{i}}(H_{i,C_{i}}-R^{i})HCH_{i}-IC_{i}-IC_{i})$	บ้	-0.92913	-0.92918	-0.92918	O	-154.40324	17716.0	0,77247	-17,61330	-17,42244	4830	131.70	21.90	1,97162	0.51388
(C'-C' (e))	(C'=C' (R'=H;C;)C;,(R"=H;C;)CH; = (C'=C' (e))	.H C.	-0 72457	-0.72657	-0.72457	-0.7245T	-(\$4.51399	0.91771	0.76765	-17.92866	617.77.71-	50.04	129.96	22.66	1.94462	0.49298
(C-C, C)	$\operatorname{ter}(C_{s}C_{s}(H_{s}C_{s}-R))HCH_{s}-(C_{s}-C_{s}(9))$	τ'3	-0.72457	-0.92918	.0.9 <u>2</u> 918	O.	-154,19863	17716.0	0.78155	-17,40869	-(7,21783	52.78	127.22	24,04	1.92443	0.47279
$IsnC_{\alpha}(R-H_{\alpha})$	$tsuc_{*}(R-H;C_{*})C_{*}(R^{*}-H;C_{*})CH_{*}-CC_{*}$	H;- C,	-0.72457	-0,72457	-0.72457	-0.72457	-154.51399	0.91771	0 76765	-17.92866	477.71.	50.04	129.96	22.66	1.94462	0.49298

	` ;	110	Š	,	21.	(e) (-)		(0)	(e))-)	(e)	(C)
	Group	(ii) Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	-	1	3	2	-	-	-	-	_	1	-
",	0 .	0	2	1	0	0	٥	0	٥	٥	0
11,	0	0	0	0	0	0	0	0	c	0	0
	0.5	0.5	0.75	6,75	0.75	0.5	0.5	0.5	5.0	0.5	5.0
1	-	-	1	_	-	-	-	-	-	-	-
۲,	7	-	1	1	-	-	~	-	-	-	-
	0.77087	0.77087	0.91771	17716.0	17216.0	17716.0	17716.0	17716.0	0.91771	0.91771	17716.0
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	0.5	0.5	0.75	0.75	0.75	5.0	5.0	0.5	0.5	0.5	0.5
. 2	-	-	1	-	1	-		-	-	-	-
V, (aV)	-32.02108	-32.02108	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (aV)	10.37015	10.37015	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	937773
(eV)	4.30097	9,30097	32.53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
(cV)	-4.65048	-4.65048	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(w m) (cV)	-14.63489	-14,63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
ΔΕ _{ηνισ} ί.σ.π) (eV)	0	0	0	0	0	0	0	0	0	0	0
Er (. 11 11) (cV)	-14.63489	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
E. (n. 10) (aV)	-31.63534	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31,63535
i_{r} $\left(ainm - ainm, nivp', AO\right) (eV)$	-2.69892	-2.69892	0	0	. 0	-1.85836	1.85836	-1.44915	-1,85836	-1.44915	-1,44915
$\mathcal{E}_{\tau}(m)$ (cV)	-34.33429	-34.33429	-67,69450	-49.66493	-31.63537	-33,49373	-33.49373	-33,08452	-33.49373	-33.08452	-33,08452
w (10th rad/x)	24.8506	12.9435	24.9286	24.2751	24.1759	9.43699	669876	15.4846	9.43699	9.55643	9.55643
E _k (eV)	16.35707	8.51966	16.40846	15.97831	15.91299	6.21159	65112.9	10.19220	6.21159	6.29021	6.29021
$\vec{E}_{\rm p}$ (eV)	-0.27472	-0.19826	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0,16416
Fire (UV)	0.13849	0.10911	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978 [4]	0.09944	0.12312	0.12312	0.12312
β (σV)	-0,20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
15, (smm) (BV)	-34.53976	-34,47800	-67.92207	-49,80996	-31,70737	-33.59732	-33,49373	-33,24376	-33.59732	-33.18712	-33.18712
E (c, to no) (cV)	-14.63489	-14.63489	.14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
Fuend (10 181) (cV)	0	0	-13.59844	-13,59844	-13.59844	0	0	0	o	0	0
E. (a-) (aV)	5.26998	5.20822	12.49186	7.83016	3,32601	4,32754	4.29921	3.97398	4.17951	3.62128	3,91734

Table 15.3). The total bond energies of branched-chain alkyl fluorides calculoted using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy E at that is subtracted from the

Formula	Name	C-F (i) C-F (ii)	C-F (ii)	CH,	CH;	H.)	C ~ C (a)	(e) U=U	(a) 2-2	C-C (q)	(e) C-C	(J) C-C	Ω.	Calculated Total Bond	Experimental Total Bond	Relative Print
	Tetralluoromethane	4		٥	o	c	0	0	6	G	c	6	-) OTOG	١.	00000
	Trifluorumethane	-	-	•	•	•	•	. ,		. ,	•			*****		2000
		1	•	•	•	-	>	•		-	0	0	-	19.28398		0 00000
וייין ייין	Difluoromethans	~	0	•	-	0	0	0	0	•	0	0	c	210011		20000
	I-Fluoropropane	0	-		~	٥	7	-	c				, –	41 92746		1000
C,H,F	2-Rugnopropane	•	_	•		-			, ,	•			•	41.40/43		0.0004

angs parameters of or			Ľ		3500	ייים באלהיייה	Hall Values [1],	no carcination	, , , , , , , , , , , , , , , , , , ,	in in a land			1	Cy 13 27 (, mon-1	Or of	.	-	,
Rend 2 Lowieral Creatender	Townward Arms Hybridization	Crestorte Hybridization	Hybridization		Erander Armen		Hybridization	اً ئ	<u>ر</u> ک	ن- ت	ن ن	ۍ.	v	rp ;	ø, ;	6 - (or::		EXP. 0
(a,) Aleas Decignation (a,) (Co,) (Table 15.3.A)	(O _c) (Table 13.3.4)	Designation (Table 13.3.4)	Designation (Table 13.3.A)	 [_	Designation (Table 13.3.A)							(<u>)</u>	<u> </u>				D
-16.17521 F	43128 -16.17321 12 -16.17521	-16,17521 13 -16,17521	12 -16.17521	-16.17521 F		1	5	0.84115	0.84[15	-	-	-	0.84115	-1.44915			=	110.53	108.8 (fluoroform)
211106 2.62403 3.8387 -17.10440 31 -17.4282	3.8987 -17.10440 31	-17.10410 C. 31	11		-17.42282 Ji)	Ŀ	0.79546	0.78092 (Eq. (15.64))	6.73	-	57.0	2718873	0			-	110.38	
291547 26260 4.5826 - C. 23 25 4.5828 G. C. 25	4,5826 -16 68412 25	-16.68412 25 C _A 25	13		-17.42382 F		ts.	0.81549	Q.77087 (Eq. (15.110))		-	_	0.79318	-1.85836			=	111.53 (1,2~	110.3 (1,2-difluoroeihane)
2.201547 2.11106 4.1633 -15.55933 S -(4.82575	4,1633 -(15,5593) 5	-(5.5503) S	s		-(4.82575 C,		-	0.87495	0,91771	0.75	_	27.0	1.04687	•			-	110.83	111.0 (1,1-difluoroethane)
Z11106 211106 34252 -15.75493 7 H	3 4252 -15.75493 7	-15.75493 7	,		π			0.86159	1	-	-	0.75	1.15796	0			2	108.44	(prepare)
															69.51		= .	110.49	112 (propane) 113.8 (buiane) 110.8 (tobuiane)
						, ,									69.51		1	110.49	111.0 (butane) 111.4 sobutane)
2.09711 2.09711 3.4252 -15.73493 7 H	3,4252 -15,75493 7	-15.75493 7	,		r			0,86359	1	-	1	0.75	1,15796	0			2	109.50	
															70.S6		01	109.44	
															70.56	-	2	109.44	
201547 201547 4.7058 -16.05412 25 C.	4,7958 -16.68411 25	-16.61412 25	23		-16.68412 C;		25	0.81549	0.81549	-	-	_	0.81549	-1.85836			=	110.67	110.8 (ixobutane)
291547 2.11323 4.1633 C. C. C.	4,1633 (', 5	-15,55033 S	s		-14.82575 (',		1.	0,87495	0.91771	0.75	-	0.75	1,04887	0			=	110.76	
291547 2.09711 4.1633 (5.55033 5 -14.82577 C. C.	4.1633 -15.55033 5	.15.55033 C.	8.		-14.82575 (",	, ,	 .	0.87495	0.91771	6.73	-	0.75	1.04887	0			=	72111	111.4 (fsobutane)
2,90127 2,90127 4,7958 15,55013 5 -14,82575 C,	4.7958 -15.55033 S	.15.55033	٧.		-14,82575 C,		_	0.87495	12210'0	0.75	-	0.75	1.04887	-1.85836			=	0 42111	(isobutane)
															72.50	-	2	107.50	

ALKYL CHLORIDES
$$(C_n H_{2n+2-m} Cl_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$$

The branched-chain alkyl chlorides, $C_n H_{2n+2-m} Cl_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a chlorine. The C-Cl bond comprises a functional group for each case of Cl replacing a H of methane for the series $H_{4-m}C-Cl_m$, m=1,2,3, with the C-Cl bond of CCl_4 comprising another functional group due to the limitation of the minimum energy of Cl matched to that of the $C2sp^3$ HO. In addition, the C-Cl bond due to Cl replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2CH)$ and t-butyl $((CH_3)_3C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Cl functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the Cl AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chorine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq.

20 (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the Cl AO has an energy of $E(Cl) = -12.96764 \, eV$. To meet the equipotential condition of the union of the C - Cl H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the C - Cl-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Cl\right) = \frac{E(Cl)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317\ (15.110)$$

The valence energy of the carbon 2p is $-11.2603 \, eV$ and that of the Cl AO is $-12.96764 \, eV$. The energy difference is more than that of $2E_r(C-C,2sp^3)$ given by Eq. (14.151) for a single

bond. Thus, $E_r(atom-atom,msp^3.AO)$ of the C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is $-1.44915\,eV$ based on the energy match between the $C2sp^3$ HO and the Cl AO corresponding to the energy contributions equivalent to those of methyl groups, $-0.72457\,eV$ (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each 10 $E_D(Group)$ of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHCl group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CCl group (no H bonds to C) were 15 each treated as a tert-butyl C-C. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

Functional Group	Group Symbol
CCl of CCl _m H _{4-m}	C-Cl (i)
. CCl of CCl ₄	C-Cl (ii)
CCl of $C_n H_{2n+2-m} Cl_m$	C-Cl (iii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

F	Group	2.10725	1.45164	1.53635		1.532	1.532 (propane)	1.532 (propane) 1.531	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane) 1.52750
(e) D-C	Group	2,10725	1,45164	1.53635		1.532	1.532 (propune)	1.552 (propene) 1.531	1.532 (propane) 1.531 (butane)	1.532 (properte) 1.531 (bulane) 1.52750
C-C (d)	Group	2.12499	1.45744	1.54280		1.532	1.532 (propane)	1.532 (propane) 1.531	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane) 1.54616
0-7-2	Group	2,10725	1.45164	1.53635		1.532	1.532 (propane)	1.532 (propanc) 1.531	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane) 1.52750
(J-C (B)	Group	2,12499	1,45744	1,54280	_	1.332	1.532 (propene)	1.332 (propene) 1.531	1,532 (propane) 1,531 (butane)	1,532 (propene) 1,531 (bulane) 1,54616
(B)	Group	2.12499	1.45744	1,54280		1.532	1.532 (propane)	1.532 (propsne) 1.531	1.532 (propane) 1.531 (burane)	1.532 (propane) 1.531 (burane) 1.54616
	Group	1.67465	1.05661	1.11827			21.12	(isobulano)	. 1.122 . (isobutano)	(isobutano) 1.29924
(no) n	Oroup	1,67122	1.05553	1.11713		1.107	1,107 (<i>C - H</i> propane)	1,107 (C-H propane)		1.107 (C-H propare) 1.117 (C-H butane) 1.29569
	Oroun	1.64920	1.04856	1.10974		1.107	1.107 C – H propane)	1.107 C – H propane) 1.117	1.107 C - H propane) 1.117 C - H butane)	1.107 C - H propane) 1.117 C - H butane)
	Group	2,32621	1.69136	1.79005		1.802	1.802 (ethyl chloride)	1.802 (ethyl chloride) 1.790	1.802 (ethyl chloride) (1.790 (1.3-dichlorochanc) (1.3-dichlorochanc)	1.802 (ethyl chloride) 1.790 (1.2-dichlorrechane) 1.59705
American C-C (i) C-C (ii) C-C (ii) C-C	Grand	2.37026	1.70729	1.80692			1	1.767 (carbon karachlorida)	ğ.	1.767 (carbon retrachlorido) 1.644 16
יוופ הפחווברו הפון	Group	2.32621	1,69136	1.7900\$			1.785		ide)	
		(10,)	(°)	Bond	₹ .:	(F)	rp. Bond	r. (A)	2c' (A) Exp. Bond Length (A)	2c' (A) 2p. Bond Length (A) h,c (a)

Table 15.35. The MO to HO Intercept geometrical bond parameters of branched-chain alkyl chlorides. H. N. H. are H or alkyl groups. E; is E. Crom - nion, mip*AO).

								-							
Bond	Atom	k;, (eV) Bond 1	آئہ (ھV) Bond 2	/i, (eV) Bond 3	E _r (eV) Bond 4	Final Total Energy ('24p' (eV)	(a _a)	(a,)	(eV) Final	E(C22p) (eV) Final	θ. (•)	·(o)	(a)	d, (a,)	(σ_{\bullet})
$H_{s=0}(t_s - (T_s, m = 1, 2, 3, (t_s - (T_s)))$	ن	-0.72457	С	0	ū	-132 34026	0,91771	0.87495	-15.55033	-15.35946	69.62	110.31	30,00	1.90599	0.30463
$H_{L_m}C_+ - (T_n, m = 1, 2, 3, (C_n - CT (3)))$	٥	-0,72457	Q	0	O		1.05158	0.87495	-15.55033		29'69	16.031	30.90	1,59599	6.30463
(C, -CT (fi))	ť.	יה, גונהו אין	U	0	U	-152,08028	17716.0	· 0.RBDR3	+6062'51-	-15.D954R	RC.00	113.02	29.87	2.05530	0.34801
(נ." –נ.ו (!!) נ."נו	1.5	-0,46459	0	b	U		1.05158	0.88983	-15.29034		66.9R	113.02	29.87	2.05530	0,34801
((;;) (;;) ((;;) –(;) (;;)	ن'	-0.72457	K16Z67)-	U	υ	-153,26945	1,7119,0	0,42362	-16.47951	-16,28K4	63.18	116.82	27.48	2.06384	0,37248
(C, -C7 (ii)) -H,C,C, -C7	خ	-0.72457	0	c	U		1.05151	0.8749.5	-15.55033		29'69	110.38	30,90	1,99599	0.30463
C-H (CH,)	i	A 92918	0	0	0	-152.54487	17116.0	0.86359	.15.75493	-15.56407	77.49	102.51	41,48	1,235rd	0.18708
('-H (CH ₂)	<i>L.</i>	40.92918	-0,9291R	u	U	153.47406	0.91771	0,81549	-16.68412	-16,49325	68.47	111.33	35.84	1.35486	0.25/33
(H.) H)	C	-0,9 2 918	-(192918	H1020.0-	U	154.4TG3A	17719.0	0.77247	-(7.61330	.17,42244	61.10	118.90	31.37	1,42988	0.37326
H,C,C,H,CH; H,C,C,H,CH;	٠, ١	NI USU.D.	D	c	0	-152.54487	17719.0	0.84359	-15.75493	-15.56407	63.82	116.18	30,08	97.858.I	0.31106
H,C,C,H,CH,	ئ	ж1626.0-	# 16Z6'U-	С	С	153,47406	144160	0.81549	-16,68412	-16.49325	36.41	123.59	36,06	1,90290	0,45117
$R-H_{\mathcal{L}}(\mathcal{L}_{+}(H_{\mathcal{L}},-R)HCH_{+}-R)$	٠	\$10Z6.0-	41,9291%	810 <u>5</u> 0.0.	O	-154,40334	0.91771	0,77247	-17,61330	LIT.4224	41.30	(31.70	21.90	1.97162	0.51388
$R = H_1C_n(R^2 - H_2C_n)C_n(R^2 - H_2C_n)CH_1 - (C_n - C_n)$	ď	-0.9291x	-U 72457	15127.0-	15451.0-	0.54.71860	0,91771	0.75189	99826'21-	9.17.7.1.	48.21	131.79	21.74	1.95734	0.50570
$Rod^{*}(C_{\mu}(H,C_{\mu}-R))HCH_{\mu}-$ (C_{\mu}(C_{\mu}(G))	ť	-0.92918	-4,9291R	810 <u>5</u> 2.0-	c	-154,40324	0,91771	1ענד.0	-17,61330	+17,42244	48.30	131.70	21.90	1.97162	0.51388
$(C'-C')$ $(R'-H_2C_*)C_*(R'-H_3C_*)C_{R_*}$	C.	-0,72457	-0,72457	. 72LCT.0-	13457	-134.51399	17710.0	0.76765	-17.92866	ettet.51-	50.04	96'621	22.66	1.94462	Q.49298
(כ.–כ. (נ) ומע,'ל.'(H'ל.' – א.)HCH" –	رد	-0.72457	ж1026.0-	#16Z6.0-	હ	-154.19863	0.9177[0,78135	-17.40169	-(7.21783	52.78	127.22	24.04	1.92443	0.47279
$ksc'_{*}(R-H_{3}C_{*})C_{*}(R^{*}-H_{2}C_{*})CH_{3} (C-C^{*}(0))$	ť	-0.72457	-0,72457	-0.72457	-0.72457	154,31399	0,91771	0.76765	-17,92166	-17.73779	\$0.0£	129.96	9977	1.94462	0.49298

Parameters	0-0	0-7	נייני	1	1	77	17 0 0					
	`∈	; :	<u></u>	÷.	;; ;	ב נ נ	(a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	(a)	(E)	(g)	(a)	(e) U-U
	Group	Group	Group	Group	Group	digni	dippi 5	685	die S	Granp	Group	Group
η,	_	_	1	9	7	_	-	-	-	-	-	-
n,	0	0	0	. 2	_	٥	0		•	. 6		-
n_{r}	0	0	c	0	٥	0	٥	0	0			
<i>C</i> ,	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	50		, ;	2
	0.81317	0,81317	0.81317	_	-	-	-	-	-	-		} -
c,	-	-	_	-	-	-	-	-		-		- -
J*	-	_	-	17716.0	0.91771	17716.0	0,91771	0.91773	0.91771	17710	001771	0.01771
5,	-		-	0	_	-	0	0	0	-	-	
c,	2	7	2	_	 -	-	2	2	2			,
c,	0	0	٥	e	2	_	0	0	0	0		
. 4	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	
12	0.81317	0.81317	0.81317	1	-	-		_	-	_	-	-
V, (aV)	-29.68411	-28.95265	-29.68411	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29 10112
V, (aV)	8.04432	7.96922	8.04432	38.92728	25.78002	12.87680	9.33352	9,33352	9,37273	9.33352	9.37273	9.37273
T (aV)	6.38036	6.10748	6.38036	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6 77464	00400	6 90 500
V (aV)	-3.19018	-3.05374	-3.19018	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3 45750
El.v m] (aV)	-14.63489	-14,63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15,56407	-15.35946	415 35946
ΔΕ _{π, νιν} (.v. nr) (αV)	-1.44915	-0.92918	-1.44915	•	0	0	0	0	·	0	0	0
E, (.v. vo) (c.P.)	-13.18574	-13,70571	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15 35946	14 3404K
$E_T(u_j, m)$ (cV)	-31.63536	-31.63540	-31.63536	-67.69451	49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	31 6933
E. (atom - atom, nxp? A() (cV)	-1.44915	-0.92918	-1.44915	0		٥	-1.85836	-1.85836	-1.44915	-1.85836	-1 44915	-1 44915
F, (w) (cV)	-33.08452	-32.56455	-33.08452	-67.69450	49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-13 40373	-33.08467	132 08447
@ (101; red/s)	7.42995	7.22380	13,0612	24.9286	24.2751	24,1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
F. (eV)	4.89052	4,75485	8.59708	16.40846	15,97831	15.91299	6.21159	6.21159	10,19220	621159	6 29021	1,000,9
E, (eV)	-0.14475	-0.14048	16161.0-	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	218810	216416	0 15415
Fx (a1')	0,08059	0.08059 [12]	0.09113 [E1]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12512	0.17978	0.09944	0,12312	0.12512	0.12312
$E_{cc}(aV)$	-0.10445	-0.10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eng (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. 6-1 (cV)	-33.18897	-32,66473	-33.23086	-67,92207	96608'67	-51.70737	-33.59732	-33,49373	-33.24376	-33,59732	-33.18712	-33.18712
Eural la, et ses) (cV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489
Emale, et mil (eV)	٥	0	0	-13,59844	-13,59844	-13.59844	0	٥	0	0	0	0
Enternal (eV)	3.77116	3,39496	3,96108	12.49186	7.83016	3,32601	4.52754	4.29921	3.97398	4.17051	361695	3 01734

	Relative	Ē	j		0.00123	0.00217	0.00499	0.00209	-0.00138	-0.00112	-0.00028	0.00044	-0.00104	-0.00085	-0.00037	0.00034	-0.00069	0.00037	0.00002	-0.00038	0.0000	0.00000	
	Experiment	78	Total Bond	Energy (eV)	13.448	14.523	15.450	16,312	28,571	127.06	40,858	52.903	52.972	52.953	53.191	65.061	65.111	65.344	65.167	77.313	101,564	150,202	
	Section desired		Duon Bond	Cuerzy (ev)	13.43181	14.49146	15,37248	16,26302	28.61064	40.76834	40.86923	52,92604	\$2,02693	52.99860	53.21057	65,08379	65.15630	65.36827	65.16582	77,34233	101.55684	150.87640	
	E	ř			-	÷	0	0	0	0	0	0	0	0	7	c	0	-,	0	0	0	0	•
	<u>د</u> :				0	0	0	0	0	0	0	0	c	0	0	o	0	0	0	٥	0	c	
	<u>،</u> ن				•	0	•	0	0	•	•	•	0	0	c	0	0	0	0	0	0	0	•
	(a) 1-1 (b) 1-1 (c) 1-1 (d) 1-1 (d) 1-1 (e)				٥	•	0	0	0	0	0	0	0	0	0	0	0	۰.	_	0	c	0	_
	(i)				0	c	0	0	۰ ۵		0	0	0	0 -	- ·	5 (٥,	~ (۰ د	5 (٥.	۰ د	
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	(u) -1 - 1				۰ د	5 1	، د	۰ د	.	٠,	۰,	٠, .	- ,		۰,	.		- 0	.	٦,	٠:	= •	
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DETAL				ctrachlorumethane	richloromethane	Orchloromethane	hloromethine	Chloroethane	Chloropropane	Chloropropane	Chforobutpane	Chlorobutane	-Chloro-2-methylpropane	Chloro-2-methylpropane	1-Chloropentane	Chloro-3-methylbutane	-Chloro-2-methylbutane	Chloro-3-methylbutane	-Chlorohexant	1-Chlorooctane	Chlorododecane	Chlorocudecane	
				JU JUJ	-			_											בי האים	_	÷	Ť	

	Exp. θ (•)	(dichloren ettane) (1113 (chkroform)		(DRC/H obylehlarida) 11998 (DRC/H obylehlarida)		(ch)1 defonite) (1,1 defonitationalistic) (1,2 defonitationalistic) (1,3 defonitationalistic) (1,4 defonitationalistic) (1,1,1 defolieradistic) (1,1,1 defolieradistic) (1,1,1 defolieradistic)	1)R6 (Shyf dileride)	103 (tappens)	(Prinysse) (Prinysse) (13.8 (Prilos) (10.8 (Ferfuttane)	(11.0 (Pulane) 11.1.4 (jeelappoo)				(fig.8 (isothutana)		111,4 (behintme)	111.4 (isobuture)	
	<u> </u>	111.40	31.16	109.50	P# 601	100.61	110.83	108.44	110.49	110.49	62 50	109.14	13 601	110 67	110.76	111 27	111.27	OZ.701
	9.0											Ī						
	(3.																	
ا خ	, (°,				70.56				69.51	15.49		70,56	72 05					8.5
ra – crom.msp³./	Ε _τ (eV)	K162619-	c	e e		41,929 14	c	0		:	c			-1.85836	0	æ	-1.85836	
Er is Er (are	۶,	144160	£.09775	1.15780		Q R6339	1,04887	1.157%			1.15796			0.81549	1.04587	18870'1	1,04887	
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he preceding an	ť	081317 (Eq.(15.111))	(Gr () 3 v3))) 0 82310	-		ακ1317 (Eq. (15.111))	-	-			-			-	-	-	1	
uneters from th	ئ	-	67.0	-		-	81.11	-						1	87.0	6.75	87.78	
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nd experimen		17 K2575	-12,96764 (7)	11		-12,9,764	-1416573	Ξ			11			;) Elbennia	4.7 5.7	-(4,82575	,14,XZ575	
sikyi chlorides s	Atast I Hybridizeken Derignateru (Tahle 15.1.A)	- '	89	,		-	·n	,						ก	*	ş	3	
ched-chain a		7.7 7.7	.16 27490	-15.75493		-15.75203 C.	.15.53m;	-15.75.97			15.75.93			Janasari C,	15.5903	-15.53013	.15.58833 f.	
rs of bran	(a,)	S, STP9	1765.1-	34252		1,1539	4.1633	3.4252			3.135			A. TUSK	ז נענו	4,1633	4.7958	
de paramete	, zc. (a,)	1,756,8	1,38,771	2,1971.1		3,30271	2.11806	3,1141%			111,607			נופופב	21123	11202	TEENTZ	
are pood	2¢' Bwd! (a,)	1,34071	3.11.0%	1177711		7316.2	1,91547	2,1130%			1117001			191547	2,91547	2,91347	2,90,527	
Table 15.38. The bond angle parameters of branched-claim alkyl chlorides and experimental values [1]. In the calculation of θ_c , the parameter from the preceding angle were used. E, is E, are a commany AO)	Man of their	(נג'' –נג (נ)) לנג'' –נג	(C, -(7 (iii))	ДНС,Н ДНС,Н ((C, —C7 (III))	((!!) //-'())	((ij)(.)) (2'.1)	CC, - CT (W))	H. H.	255.7	Н.З.Д	H".JH7	ZC,C,C.	H'.1'.77	<i>ط</i> :ررز سرز	ZC,T,H	ZC, C, H	יייונ" ענ"נ"נ"	15.5.7

ALKYL BROMIDES $(C_n H_{2n+2-m} Br_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$

The branched-chain alkyl bromides, $C_n H_{2n+2-m} Br_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by a bromine. The C-Br bond comprises a functional group for each case of Br replacing a H of methane for the series $H_{4-m}C-Br_m$, m=1,2,3, with the C-Br bond of CBr_4 comprising another functional group due to the limitation of the minimum energy of Br matched to that of the $C2sp^3$ HO. In addition, the C-Br bond due to Br replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Br functional groups comprises the hybridization of the 2s and 2p shells of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ hybridized orbital (HO) and the Br AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and 20 proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the Br AO has an energy of $E(Br) = -11.81381 \, eV$. To meet the equipotential condition of the union of the C-Br H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the C-Br-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } Br) = \frac{E(Br)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.74081 \quad (15.112)$$

The valence energy of the carbon 2p is $-11.2603 \, eV$ and that of the Br AO is $-11.81381 \, eV$. The energy difference is less than that of $E_T(C-C,2sp^3)$ given by Eq. (14.151) for a single bond. Thus, $E_T(atom-atom,msp^3.AO)$ of the alkyl C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.92918 \, eV$ (Eq. (14.513) based on 5 the maximum single-bond-energy contribution of the $C2sp^3$ HO. $E_T(atom-atom,msp^3.AO)$ of the series CBr_mH_{4-m} m=1,2,3 is equivalent to those of methyl groups, $-0.72457 \, eV$ (Eq. (14.151)). For CBr_4 , $E_T(atom-atom,msp^3.AO)$ of the C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is $-0.36229 \, eV$ (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1, $E_T(atom-atom,msp^3.AO)=-0.72457 \, eV$

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHBr group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CBr group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane, E_{mag} is positive since the terms due to the two bromine atoms cancel that of the t-butyl and CH groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

Functional Group	Group Symbol
CBr of $CBr_m H_{4-m}$	C-Br (i)
CBr of CBr ₄	C-Br (ii)
CBr of $C_n H_{2n+2-m} Br_m$	Ċ−Br (iii)
CH₃ group	$C-H(CH_3)$
CH₂ group	$C-H(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

0.49298

0.47279 0.49293

27,00

0.36734

0.33413 0.33413

> 2.16RDN 2,21357 221357 1,21237 2.14337 1,23564

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1.3548.6 1.42788

LESKIN 1.90%30 1.97162 1.95734 1.97162

0. IN70X

0.45117

0.51388 0.50570 0.51388

Table 15.40.	able 15.40. The geometrical bond parameters of branched-chain alkyl	d parameters of branc		brownides and experimental values	i values [1].							
Parameter	() ()	C-Br (ii)	C~Br (iii)	(H.J) H)	(.H.)	æ-:	(E) ()-()	(a) U-U	(e) U-U	(g) U-U	(e) U-U	(£) U-U
	Green	. Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
a (a.)	2,49163	2.52509	2,47529	1.64920	1.67122	1.67463	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c. (a)	1.83395	1.84622	1.82719	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1,45164	1,45164
Bond Length 2c' (A)	1,94097	1.953%	1,93381	1,10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	(.53633	1.53633
Exp. Bond			1.93	1.107	1.107		1,532	1.532	1.532	1.532	1.532	1.532
Length	1.933 (methyl bromido)	1.935 (carbon tetrabronsida)	(1.1.1-tribromocthane)	(C - H propans)	(C - H propane)	1.122 (isobutane)	(propane) 1.531	(propane)	(propane)	(propane)	(propane) 1.531	(propane)
₹			(1.2-dibromocthane)	(C-H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(butanc)	(butanc)
b, c (a,)	1.68667	1.72265	1.66689	1,27295	69567.1	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
	0.73604	0.73115	0,73877	0.63580	0.63159	0.63095	0.68600	0.68500	0.68888	0.68600	0,68888	0,68888

August (°, °, °, °, °, °, °, °, °, °, °, °, °, °	f., (eV) Bond I A.36229 4.36229	. (§ %.	(e ^y 1 ^y	- F		1			75.00	.	6	
m=1,2,3	-0.36229 -0.18114	7 2000	Band 3	(eV) Bond 4	('2sp' (eV)	(a,)	(a,)	(eV) Final	· (eV) Final	(•)	· C	(•)
m=1.2,3.	-0,36229 -0.18114	u	С	0	151,97798	17716.0	0,82582	-15,18804	11,99717	68.10	06:111	20.52
	-0.18114	5	o	0		1.15169	0,89582	-13,18804		68.10	111.90	20.02
		u	0	0	-(51,79613	17716.0	D.90664	-15,006.89	-14 11/03	64.10	113.90	28.76
2 H	4.18114	o	c	U		1,15169	P9906'0	-13,00689		64.10	113.90	28.76
Hr.	-0.46459	-0.9291R	0	0	-153,00946	17719,0	0.ИЗИК5	-16,21952	-16.02866	62.67	117,53	26,55
U U U	-0,46450	ı,	0	c		1.15169	O.HRURIS	-15.29034		69.19	110,81	27.93
.,	-0.9291R	0	۰	c	-152.54487	17716,0	0,86359	-15.73493	-15,56407	QF.TT	12,201	£. £
J	-0.9291X	#19Z9.0-	•	c	-153.47406	17416.0	081549	-16.68412	-16.49325	C#,47	111.53	35,84
	40.9291K	*11676'D+	A1059.II.	С	12E01751	17116.0	0.772.47	-17,61350	-17,42244	61.10	11R.90	31.37
H_1^{ζ} , L_2^{ζ} , H_3^{ζ} , $H_3^{-\zeta}$, $H_3^{-\zeta$	41.9291R	0	o	U	LUPPS 751-	17736.0	0.146359	-15.75493	-15,56407	63.82	116,18	30.08
:	A11020,0.	-0,929f3	•	С	-153,47406	177160	0,81549	16.68412	-16.49325	\$6.41	65.621	26.06
-n')H(H; -	.0,92018	.0 9291X	.0.9291Ж	C	72504.121-	0,91771	0.77247	-17,61330	17,42244	48,30	131.70	21.90
4,C,)(14, - C,	H1620.0-	-0.72457	-0.72457	-0.72457	03817,421-	0,91771	0.75889	-17,92866	47.57.71-	48.21	131.79	21.74
	A1050.0-	# 16Z6 ()*	# J020.0.	U	72507'751-	0.91771	0.77247	02819.71-	17.42244	41.30	131.70	21.90
$C_s(CH_3 - C_s)$	-0.72457	-0,72457	-0.72457	-0.72457	66E15,121-	0.91771	0,76765	57826,71-	47.71.	\$0.04	129.96	22.66
, C.	6,72457	-0,92918	ж] <i>62</i> 6'0-	φ.	-154,19863	171160	0.74155	17,40869	-17.21783	\$2.78	127,22	74.D4
ind., (R'-H.C.)C, (R'-H.C.)CH	-0,72457	£12457	-0.72457	-0.7245T	-154,51399	17419.0	0.76763	17.92866	¢47.71.	30.04	129.96	22.66

Parameters C~Br C-Br C-Br C	C-Br	· C-B	C-8r	CH,	.# <u>C</u>	H-2	C-C (a)	C-C (b)	(e) U-U	C-C (d)	(a) 2-2	(J) C-C
	Group Group	Group	(iii) Group	Oroup	Group	Group	Group	Group	Group	Group	Отопр	Circuit
u_1	-	-	-	3	2	-	1	1	1	-	1	-
a,	0	0	۰	2	-	0	0	0	0	0	0	0
ñ,	С	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	. 0.5	0.75	0.75	0.75	0.5	50	0.5	0.5	0.5	0.5
5	0,74081	0.74081	0.74081	-	-		1	1	-	_	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
	-	-	-	.17719.0	17716.0	0.91771	0.91771	17716.0	17716.0	17716.0	17716'0	17716.0
ડે	0		0	0	1	1	0	0	0	1	1	0
v	7	2	7	1	_	ı	2	7	7	2	7	7
	0	0	0	£	2	1	0	0	0	0	0	0
ر؛	2.0	0.5	0.5	0.75	0.75	0.75	0.5	6.0	6.5	0.5	0.5	0.5
^.	0.74081	0.74081	0.74081	1.	1	1	1	-	1	-	1	1
V, (eV)	-27.94806	-27.44996	-28.22940	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
1', (cV)	7,41885	7.36953	7.44631	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9,33352	9.37273	9.37273
T (aV)	5.60839	5.43544	5.70686	32,53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-2.80419	27.717.2-	-2.85343	-16.26957	-10,53337	16242.5-	3.38732	-3.38732	•3.43250	-3.38732	-3.45250	-3.45250
E[.o no] (aV)	-14.63489	-14.63489	14.63489	-15.56407	-15,56407	-14.63489	-15.86407	-15.56407	-15,35946	-15.56407	-15,35946	-15,35946
ΔΕ _{π,1,11} (.w m) (cV)	-0.72457	-0.36229	-0.92918	0	0	0	0	o	0	0	0	0
Er (.10 m) (cV)	-13.91032	-14.27260	-13,70571	-15.56407	-13,56407	-14,63489	-15.56407	-15.56407	9865521-	-15,56407	-15,35946	-15.35946
Ethina) (cV)	-31,63533	-31.63531	-31.63537	-67.69451	-49.66493	-51.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$I_{i,p}^{*}\left(alom - alom, misp^{3}, AO\right)\left(cV\right)$	-0.72457	-0.36229	-0.92918	0	0	0	-1.85836	95858'1'	-1.44915	-1.85836	-1,44915	-1.44915
E, (se) (eV)	-32,35994	99266.15-	-32.56455	-67.69450	-49.66493	-31,63537	-33.49373	-33,49373	-33.08452	-33.49373	-33,08452	-33,08452
(10" rad 1.5)	6.39733	6,27039	6.45864	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	6,55643	9,55643
E_{κ} (eV)	4.21083	4,12741	4,25777	16.40846	15.97831	15,91299	6.21159	651129	10.19220	621159	6.29021	6.29021
Γ, (eV)	-0.13137	-0.12861	-0.13293	-0.25352	-0.25017	-0,24956	-0.16515	.0.16515	-0.20896	-0.16515	-0.16416	-0.16416
F.c. (cV)	0.07575 [14]	0.08332 [15]	0.07575	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	87671.0 [4]	18) \$\$660.0	0.12312 [2]	21221.0 [2]	0.12312 [2]
F. (eV)	-0.09349	-0.08695	-0.09506	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
F. (cV)	0.14303	0.14803.	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803
$E_T^{\{i,m_T\}}(\sigma V)$	-32,45343	-32.08460	-32.65961	-67.92207	49,80996	-31.70737	-33.59732	-33,49373	-33,24576	-33.59732	-33,18712	-33.18712
E L 11 14 (cV)	14,63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489
Eneralis vo was (eV)	0	0	0	-13.59844	-13,59844	-13.59844	0	0	0	0	0	0
F (m) (c)	3 18365	2.81482	3.38983	12 49186	7 83016	10965 5	437754	1 20021	3 97798	136217	861695	3 01724

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Table 15.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of 6, the parameters from the preceding angle were used. E, is 6, aron - atom, may 1.40].

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	ZhC,hr (C, - hr ())	ZHC, Hr ((', - Br (iii))	ZHC,H ZHC,H ((',-Br (iii))	∠C',C',H', (C', - Br (iii))	(C, - Hr (iii))	H"JH7	77.7.7	H'5'.17	Subj.	7,7,7,7	H*5.77	5, 5, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	1	7,5,37		7,50.77

ALKYL IODIDES
$$(C_n H_{2m+2-m} I_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$$

The branched-chain alkyl iodides, $C_n H_{2n+2-m} I_m$, may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by an iodine atom. The C-I bond comprises a functional group for I replacing a H of methane (CH_3I) or for I replacing a H of an alkane corresponding to the series $C_n H_{2n+2-m} I_m$. The C-I bond of each of CH_2I_2 and CHI_3 comprise separate functional groups due to the limitation of the minimum energy of I matched to that of the $C2sp^3$ HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

- The solution of the C-I functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the I AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq.
- 20 (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E\left(C,2sp^3\right)=-14.63489~eV$ (Eq. (15.25)). The I AO has an energy of $E\left(I\right)=-10.45126~eV$. To meet the equipotential condition of the union of the C-I H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the C-I-bond MO given by Eqs.
- 25 (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ I\right) = \frac{E(I)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.45126\ eV}{-14.63489\ eV}\left(0.91771\right) = 0.65537 \quad (15.113)$$

The valence energy of the carbon 2p is $-11.2603 \, eV$ and that of the I AO is $-10.45126 \, eV$. The energy difference is positive. Thus, based on the maximum charge density on the $C2sp^3$

HO $E_T(atom-atom,msp^3.AO)$ of the C-I-bond MO in Eq. (15.52) due to the charge donation from the C and I atoms to the MO is -0.36229~eV (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1, $E_T(atom-atom,msp^3.AO)=-0.72457~eV$ and $E_T(atom-atom,msp^3.AO)=0$) for methyl and alkyl iodides, -0.18114~eV for diiodomethane, and 0 for CHI_3 .

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain 10 alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each $E_D(G_{CPURP})$ of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that was subtracted from the weighted sum of the $E_D(G_{CPURP})$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHI group (one H bond to C) were each 15 treated as an iso C-C bond. The C-C bonds to the CI group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

20 Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of CH_3I and $C_nH_{2n+2-m}I_m$	C-I (i)
CI of CH_2I_2	C-I (ii)
CI of CHI ₃	C-I (iii)
CH₃ group	$C-H$ (CH_3)
CH₂ group	$C-H\left(CH_{2}\right)$
СН	. С – Н
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

1) C - I (ii) C - I (C II) C - I (C II) C - I (C III) C - I (C IIII) C - I (C IIIII) C - I (C IIIIII) C - I (C IIIIIIIIIIIIIIIIIIIIIIIIIIIIII		_								~
		(i) D-2	Group	2.10725	1,45164	1.53635	1.532 (propane)	1,551 (butane)	1.52750	0.6888
		(e) D-D	Group	2.10725	1,45164	1.53635	L.S32 (propesse)	1,531 (butane)	1.52750	O GRRRR
		(g) 2-2	Group	2.12499	1.45744	1.54280	1,532 (propane)	1.531 (butane)	1.54616	0.68600
		(9))-2	Group	2.10725	1,45164	1.53635	1,532 (propane)	(531 (butane)	1.52750	0 68888
		(a) 2-2	Oroup	2.12499	1.45744	1.54280	(propane)	1.531 (butana)	1,54616	0 68600
		C~C (a)	Group	2.12499	1.45744	1.54280	1.532 (propane)	1.531 (butane)	1.54616	0.68600
		H-3	Group	1.67465	1.03661		1.122	(isobutane)	1.29924	0.63095
	alues [1].	("H) H-3	Group	1.67122	1.05553	. (,11713	1.107 (C - H propane)	1,117 (C-H butane)	1,29369	0.63159
10bic 13-6. The Econdinal boint parameters of transcribe-chini alivit loads Purpmeter	es and experimental v	C-H (CH.)	Group	1.64920	1.04856	1.10974	1.107 (C - H propane)	(C - H butane)	\$9272.1	0.63580
10b(c) 13.46. The geometrical bond parameters of brance C - I (i) C - I	hed-chain alkyl iodid	(m) /-3	Group	2,70662	2.03222	1		odida)	1.78770	0.75083
Bible 3.46. The teometrical bond	a parameters of branc	(1) 1-2	Group	2.68865	2.02546	2.14365	2.132	(methyl iodide)	1,76815	0.75334
Parameter o (a,) c (a,) Bond Length zer (A) Exp. Bond Length (a) b, c (a,)	The peometrical bon.	(c) /-3	Group	2.67103	2.01881	2,13662	2.132	(methyl todide)	1.74894	0.75582
	able 15.46.	Parameter		σ (a _n)	c. (a,)	Bond Length 2e* (A)	Exp. Bond	3	b,c (a,)	,

.

.

Table 15.47. The MO to HO intercept geometrical band parameters of branched-chain alkyl indides. R.R.R. are H or alkyl groups.	strical bond	parameters of b.	ranched-chain a	kyl indides. R.	R.R. are H or		E, is E, (dlom - alom, msp' AO)	4 - atom, msp'.,	£0).					i	
Bond	Atom	الما الما	T. 2	£,	F. 5	Final Total Energy	100	1	6V)	E(C24p²)	io ©	6	6,0	4	d ₂ ,
		Bond 1	Bond 2	Bond 3	Bond 4	(24p)	(_n)	(%)	Final	Final	=	=	2		
(C, -1 (i))	U	-0,1x114	a		0	-151.79583	17716.0	0,90664	-15.00689	-14,81503	69.69	110.37	29.08	2,33472	0.31560
CH,1	`	-0.18174		0	.		1,30183	0.90664	-15.00689		69.63	110.37	29.08	2,3347	031560
-#;c,c,' (c,-1 (0)	Ü	-0.1811d	-0.92914	o	0	-152.72602	17710.0	0.83377	-15.93608	-15.74521	63.16	116.84	23.22	2.40436	0.38554
(0) -H [*] C'C'1	-	-0.18114	9	0	0		130183	0.50664	-15.00589		69.63	110.37	29,08	233442	0,31560
C,H ₂ J, (C, -1 (fl))	5.	-0.09057	0	G	o	-151.70626	17116.0	0.91214	-14.91632	-14.72546	68.61	111.39	18,73	\$1856.5	0.35271
C,H,I,	`	-0.09037	۰	•	0		£310£7	0,91214	-14.91632		68.61	96,111	28.71	2,35818	0.33272
C,H, (C,-1 (iii)	ن	6	5	o	0	-151,615/79	12216.0	17716.0	-14.873373	-14,63489	67.56	112,44	28.32	2,38256	0.35035
(C, H)	`	с	a	0			1,30183	17716.0	-14.92575	-14,63489	67.56	112.44	28.32	2,38256	0.35035
C-H (CH,)	U	4) 0260.	0	0	۰	-152.54487	17710	0,86359	.15.75493	-15 36-407	77.49	102.51	41.48	1,23564	0.18768
C-H (CH ₃)	L	-0.92918	Kiuzu.a.	Б	0	-153,47400	17716.0	0.81549	-16.68412	-16.49323	68.47	111.53	35.84	1,35486	0.29933
C-H (CH)	ı	-0.92918	.0.9291R	416260-	0	P2E01*151-	17710.0	0,77247	-17,61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
H,C,C,H,CH, -	ن	-0.92918	e	С	0	.152.54487	17716.0	0.86359	-15,73493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
H,C,C,H,CH,= (G=C (a))	ť	-0.9291x	#1622.0-	o		-153.47406	17716.0	0,81549	-16.61417	-(6.4932\$	\$6.41	(11.59	90'972	1.90190	0.45117
$R-H_2C_2(H_3C_4-R)HCH_3-C_2C_2(H_3C_4-R)$	ť	-0.92918	X1620.0.	£ 3 6 2 6 '0-	0	-154 403.24	177100	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R = H_2^*C_*(R - H_2^*C_*)C_*(R^* - H_2^*C_*)CH_2^* - CC = C(0)$	ť	X1626 0-	-0.72457	-0.72457	-0,72457	-154.71860	17719,0	0.75%	-17.92866	•77.71-	48.21	62.151	21,74	1.95734	0.50570
(xoC,C,H,C,-R)HCH,-	<u>ئ</u>	-0,92918	x1626'0-	81626Tr	c	-154,40324	17710.0	0,77747	-17,61330	-17.42244	48.30	131.70	21.90	1,97162	0.51388
$(R-C_1(R-H_3C_2)C_4(R-H_3C_2)CH_3-(C-C_1(e))$:-	-0.72457	-0,73457	42457	-0,72457	-154.51399	17716.0	0.76763	-17,92866	-17,73779	50.04	129.96	22.66	1,94462	Q.49298
(c'-c'(f))	ئن	-0.72457	K1050'0+	-0,92918	ó	-154,19863	17719.0	0.7K1SS	-17.40860	-17.21783	52.7K	27.21	24.04	1,92443	0.47279
$k\kappa G''(R'-H_3C_3)C'_1(R'-H_3C_3)C'_{12}$	ن	-0.72457	.0,72457	13457	.0,734S7	-154.51599	17716.0	0.76765	-17.92866	-17.73779	\$0.04	129.96	. 22.66	1,94462	0.4929%

Parameters	7-5	1-0	7-0	CH,	CH,	H-7	(g))-)	(Q) 2-2	(a) 2~2	C-C (q)	(e) U-U	(j))-)
	Group	@ <u>G</u>	(E)	Group	Group	Granb	Group	g the b	Group	Group	Group	Group
Į,	-	-	_	3	2	-	_	-	-	_	-	-
, i	•	0	٥	2	-	o	0	o	0	0	0	٥
Ę	0	٥	0	0	0	0	0	o	0	0	0	0
ر'	0.5	0.5	0.5	0.75	0.75	0.75	6.6	0.5	0.5	0.5	0.5	2,0
ئ	0.65537	0.65537	0.65537	-	-	-	1	-	-	_	-	
دا	-	1	-		1	-	-	_	-	-	-	
· S	-	-	-	0.91771	0.91771	0.91771	0.91771	0.91771	17710	17716.0	0.91771	0.91771
5	-	0	_	0	1	1	0	0	0	-	-	0
c,	2	2	2	-	-	1	2	2	2	2	2	7
2	0	o	0	n	2	1	0	0	0	o	0	0
C.,	0.5	0.5	5,0	0.75	0.75	0.75	0.5	9.5	0.5	0.5	0.5	2,0
,	0.65537	0.65537	0.65537	-	1	-	ı	1	ı	-	-	-
V, (aV)	-26.59109	-26.34902	-26,10696	-107,32728	-70,41425	-35.12015	₹1261.82	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	6.73951	6.717.39	6.69505	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9.33352	9.37273	9.37273
T (eV)	4.97768	4.90005	4.82280	32.53914	21.06675	10.48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
V, (eV)	-2.4884	-2.45002	-2.41140	-16.26957	-10,53337	-5.24291	-3,38732	-3,38732	-3.45250	-3,38732	-5.45250	-3.45250
El.w no) (cV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
ΔΕ _{11,210} [.10 m] (cV)	-0.36229	-0.18114	0	D	0	•	0	0	0	0	0	٥
Er (, 10 un) (eV)	-14.29907	-14.45375	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15,56407	-15.35946	-15,35946
$E_r(n_i, \omega)$ (eV)	-31.63534	-31.63535	-31.63540	-67,69451	49.66493	-31.63533	-31,63537	-31.63537	-31.63535	-31.63537	-31,63535	-31.63535
$E_{\tau}(atom - atom, nisp', AO)$ (eV)	-0.36229	-0.18114	0	0	0	0	-1.85836	-1.85836	-1.44915	-1,85836	-1.44915	-1.44915
Er (sa) (eV)	-31.99766	-31.81651	-31.63537	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33,08452	-33.08452
w (10th rad / s)	10.2318	5.36799	9.90080	24.9286	24.2751	24.1759	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
E _K (eV)	6.73472	3.53331	6.51688	16,40846	15,97831	15.91299	6,21159	6,21159	10.19220	6.21159	6.29021	12067.9
E, (cV)	-0.16428	-0.11832	-0.15977	-0.25352	-0.25017	-0.24966	-0.16315	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$ec{E}_{\mathrm{Kra}}\left(eV ight)$	0.06608 [16]	0,06608	0.06608 [6]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 (2)	8797.0 [4]	0.09944	0.12312	0,12312	0.12312 (2)
E. (UV)	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E_ (aV)	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (nound (aV)	-32.12889	-31,90179	-31.76210	-67.92207	-49,80996	-31.70737	55.59732	-33.49373	-33,24376	-33,59732	-33.18712	-33.18712
Emalle, so me (aV)	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
E (4, 10:10) (0V)	0	0	0	-13.59844	-13,59844	-13.59844	0	D	0	0	0	0
E. lon (gV)	271108	10259.5	2 34429	98167 (1	7.83016	132601	75222 7	4 70071	3 073 08	4 17051	\$61.69	7.0172

Table 15.	Table 15.49. The total bond energies of branched-citain alsy! idades calculated using the functional group composition and the energies of Table 15.49. The total bond energies of branched-citain alsy! idades calculated using the functional group composition and the energies of Table 15.49.	of branched-chair	n alkyl iodides	calculated using	g the function	al group com	rosition and the	compies of 1	Fable 15.48 co	mpared to the	: experimental	values [2]. T	ne magnetic er	ergy E., that	is subtracted	from the weig	hted sum of th	c Eo (com) (
based on	sed on composition is given by (15.5	58).					į											
Formula	None	(i) 1-3) 1-2 (II) C-1 (II) C-1 (C-1 (iii)	CH,	CH_1	() HJ	CH (ii)	C-C (a)	C-C(b)	C-C (e)	CH (i) C-C (i) C-C (i) C-C (i) C-C (i)	ر-ر (و)	C-C(I)	E	Calculated Total Bond	Experimental Total Bond	Relative Error
					į											Eacrey (eV)	Energy (cV)	
Ę	Triodomethans	0	c	'n	0	e	-	o	0	c	e	-	-	-		10.33888	10.405	0.00444
GH,	Dilodomethane	0	7	c	0	-	6	0	٥.	•	0	ь	•	٥	7	12,94614	12,921	-0.00195
3	Codomethana	-	c	•	-	0	٥	•	0	•	¢	Þ	•	0	•	15.10294	15.163	0.00263
C,H,C	fodocthano	_	-	c	-	-	c	c	-	0	c	c	۰	۰	•	27,36064	27,343	99000'0
Ę,	1-lodopropano	-	c	=	_	7	0	•	~	0	c	ø	•	0		39.51834	39,516	20000
Ť	2-lodopropanc	-	•	-	7	5	-	٥	0	7	0	ç	0	0	0	39,61923	23,623	0,0000
3	2 fodo-2-methy propane	_	-	-	•	=	-	c	0	•	-	-	0	c	-	51.96057	51.890	07000

- 1			— -								_	-					
	Esp. θ (°)			1(1.2 (methyl iodife)			107 (propunc)	112 (propune) 113.8 (butane) 110.8 (isobutane)	111.0 (Pulans) 111.4 Geobatane)				1,10,8 (cardudusi)		(fsobutarc)	(isobutane)	
	j°€	112.10	gr711	109,50	103.44	111.86	2,2	110,40	110.49	109.50	109.44	109.44	110.67	110,76	111.27	111.27	107.50
	(•)																
	o, 💽		_	-		ļ					L				<u> </u>		
<u>ō</u>	0, D		_	ļ	70.56	-	ļ	18.09	0.51	_	70.56	70.56	ļ 		-		22.50
- aloni, msp'.,	(eV)	-0.36228	٥	o		8,25,5,0,	0			٥			.1.R583G			-1.85836	
Er is Er (atom	\r'	-	1.00000	1, (57%		0.87495	1.157%			1,157%			0,81549	1,04887	1,04847	1.04837	
le were used.	ر.	_	0.75	6.73		-	0.75			67.9			-	0.73	67.0	57.0	
preceding ang	<u>ن</u>	u65537 " (Eq. (15.113))	0,76115 (Eq. (15.65))	-		0,65537 (Eq. (15.113))	-						- .	_	_	-	
neters from the	ن -	-	0.73	-	ļ	-	-			-			-	0.75	67.0	0.75	
f O, the paran	C. Almai 3	_	17730,0	_		0 87495	-			-			0.K1549	17716.0	17710.0	12210	
e celculation o	C. Aven I	-	17710,0	0 146339		0.K74U5	0,863.59			0.86359			0,81549	0.87493	0.87495	0,87495	
values [1]. In th	Alon 2 Hybridication Designation	(Toble 15.3.A)	-	÷		 	π.			æ			×	 -		-	
d experimenta	Am 2	10,45126	10 45126	Ŧ		10,45126	π			н			.16.0H412	-14.82575 C,	-14.82575 C,	-14,X2373 C,	
alkyl toatdes and	Atom I Hybridization Designation	(Table 15.3.A)	-	_		~	1			1			æ	~	~	۶	
ched-chain	Final at	-10.45126	-14.82575	-15.75493		-15,55033	-15.75493			-15.75493			-tú,6#412 C.	-15.55033 C.	-15.55033 (',	-15.55033	
rs of brar	Zeries Amir (a,	6.7205	5,2203	3.4352		5.7939	3.4252	i		3,4252			4,7938	4,1633	4.1633	4.795K	
c paramete	(a) [2,2]	4 0,509.2	4,03763	2.00711		4.03763	211106			2.09711			291547	211333	2,09711	2.90327	
e bond ang	2c. (a°)	4.05092	211106	1 00111		2.91547	2.11106	_		2,09711			2,91347	2.91547	2,91547	2.90327	
Table 1550. The bond angle parameters of branched-chain alkyl foodeds and experimental values [1]. In the calculation of 0, the parameters from the preceding angle were used. E, is E, {atom - aton, mp? AO}	Afrens of Anglia	2K,1	(C, -1 (i))	2HC,H 2HC,H (C,1 (0))	(C, -1 (i))	(C, -1 (0)	Hemiters ZHC, H	מניני.	н'.5".ж	H"H7	*,1°,2',17	H", ", "	ייני ענ'ג'ני	ריי כ" ת.'נ" א	T, 1™ (." TC"C,"H	7°,°°,°°	<i>לנ</i> "נ"

ALKENYL HALIDES $(C_n H_{2n-m} X_m, n=3,4,5... \infty m=1,2,3... \infty)$

The branched-chain alkenyl halides, $C_n H_{2n+2-m} X_m$ with X = F, Cl, Br, I, may comprise alkyl and alkenyl functional groups wherein at least one H is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl H, the C-X bond comprises the alkyl-halogen 5 functional groups given in their respective sections. The alkenyl halogen C-X bond comprises a separate functional group for each case of X bonding to the C=C-bond functional group given in the Alkenes section. In addition the CH group of the moiety XCH=C comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes, $C_n H_{2n}$, comprise at least one carbon-carbon double bond comprising a functional group 10 that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are C vinyl single bond to -C(C)=C, C vinyl single bond to -C(C)=C, C vinyl single bond to -C(C)=C, and C vinyl single bond to -C(C)=C of the -C=C moiety is also an alkene functional group solved in the 15 Alkenes section.

Consider the case where X = Cl substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct C - Cl functional groups can be identified: Cl vinyl single bond to -C(C) = C and Cl vinyl single bond to -C(H) = C. The alkenyl-halide CH group is equivalent to that solved in the Hydrogen Carbide (CH) section except that $\Delta E_{H,MO}(AO/HO) = -1.13379 \ eV$ in order to energy match to the C - Cl and C = C bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) 25 functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

 $E_T(atom-atom,msp^3.AO)$ of the C=C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759 \, eV$, given by Eq. (14.247). $E_T(atom-atom,msp^3.AO)$ of each C-C-bond MO in Eq. (15.52) is $-1.85836 \, eV$ or $-1.44915 \, eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of methylene, $-0.92918 \, eV$ (Eq. (14.513), or methyl, $-0.72457 \, eV$ (Eq. (14.151)), groups, respectively.

The solution of each C-X functional group comprises the hybridization of the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl C-X-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the C-X-bond MO are each energy matched to the alkene $C2sp^3$ HO. In alkenyl halides with X = Cl, Br, or I, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. For example, the hybridization factor C_2 of Eq. (15.52) for the alkenyl C-Cl-bond MO given by Eq. (15.111) is $C_2(C2sp^3HO \ to \ Cl) = 0.81317$.

 $E_r(atom-atom,msp^3.AO)$ of the alkenyl C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is -0.72457~eV for the Cl vinyl single 20 bond to -C(H)=C C-Cl group and -0.92918~eV for the Cl vinyl single bond to -C(C)=C C-Cl group. It is based on the energy match between the Cl atom and the $C2sp^3$ HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Table 15.51. The symbols of functional group	ups of orangieu-chain aikenyl chiorides.
Functional Group	Group Symbol
CI vinyl single bond to -C(H)=C	C-Cl (i)
Cl vinyl single bond to $-C(C)=C$	C-Cl (ii)
CC double bond	C = C
C vinyl single bond to -C(C)=C	C-C (i)
C vinyl single bond to -C(H)=C	C-C (ii)
C vinyl single bond to -C(C))=CH₂	C-C (iii)
CH (alkenyl halide)	C-H (i)
CH₂ alkenyl group	$C-H\left(CH_{2}\right)$ (i)
CH₃ group	$C-H$ $\left(CH_{3}\right)$
CH₂ alkyl group	$C-H\left(CH_{2}\right)$ (ii)
CH (alkyl)	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

_							_
()-C	Group	2.10725	1.45164	1,53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
C-C (e)	Group	2.10725	1.45164	1,53635	1.532 (propare) 1.531 (butane)	1.52750	0.68888
C-C (d)	Group	2.12499	1,45744	1,54280	1532 (propane) 1531 (butane)	3.54616	0.68600
(9) 2-3	Graup	2,10725	1.45164	1,53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
(A) 2-2	Group	2,12499	1,45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	009890
(0))-)	Group	2.12499	1,45744	1,54280	1.532 (propane) . 1.531 (butane)	1,54616	0.68600
C-H (ii)	Group	1.67465	1.05661	1:11827	1,122 (isobutana)	1.29924	0 63095
(H) H-5	Group (ii)	1.67122	1.05553	1,11713	1.107 (C-R propane) 1.117 (C-R butane)	1.29369	0.63159
(H) H-J	Group	1.64920	1.04856	1.10974	1.107 (C-H propane) 1.117 (C-H butane)	1.27295	0.63580
	Oroup	1,60061	1,03299	1,09327	1,09 (nttyl chlorida)	1,22265	0.64537
(H) H-	(i) Group	1.64010	1.04566	1.10668	01.10 Correptifythm (arthur) 1.108 (arthur) 1.108 (arthur)	1.26354	0.63756
(III) ()-)	Group	2.04740	1.43087	1.51437	1.508 C: societyteses)	1,46439	0.69887
思して 一色して	Group	2,04740	1,43087	1,51437	. 1.50 8 (2-hucne)	1,46439	0.69887
	Group	2.04740	1.43087	1.51437		1.46439	0.6987
CEC	Group	1.47228	15997.1	1,34052	1.342 (2- mathylocyans) 1.346 (2-hume) 1.349 (1.34mstellarie)	0.75055	0.86030
0-0	(ii) Group	2,19358	1,64243	1,73827	1,730 (varyt chloride) 1,73 (1,1- dechloroedydcae	1,45403	0.74874
Parameter C-Q (i) C-Q C=C ('-('(i)	Graup	2.15818	1,62912	1.72419	1,730 (vinyl chlorida) 1,73 (1,1- dichlurochylene	1.41552	0.75486
Parameter		0 (0,)	0, (0")	Bond Length 2c" (A)	Exp. Bond Length (A)	6,5 (0,)	v

THE TOTAL OF THE WOLD HOUNGED Beamerings one parameters of practiced-chain mixeryl chondes. If R. R. are H or alkyl groups,	emca bon	o parameters of	branched-chain	akenyi chlonde	K,K,K are	H or siky! grow	UDS. 6, 19 6,	Er is Er (alom - alom, mg) . AO	nw40).						
noo .	Atam	ar i	₹.	ŕŁ	4	Final Total]	į	(cht)	E(C249)		6,	θ,	6	. 6
		(eV) Bond 1	Bond 2	(cv) Bond 3	Bond 4		(a.)	(°)	(eV)	(eV)	ε	€	€	<u>ૈ</u>	₹
$(\mathcal{O}(HJ)H-HJ)$	ن	1.34946	7545.0	-		(va)	0.91771	02180	.16.68413	362079	25.00	10.00			
	į		0,4,6		,					2		in var	6	1,41033	
(C, -C1 (i))	;	V (41.7)	(CPC/)+	-	-	-155 +1400	481711	0.XIX	-16 68412	-16.49315	36	100'21	X S	1.71872	0.1436
-C, = C, (H)C! (C', - C'! (J))	<i>t</i> :	הנינדה	e	c	a		1.05158	0.87495	.15.55033		R5.36	25.25	18.03	1.6995	0.0708
(c," - c, (g)) -(." = (,"(c,)(.)	Ů,	1.13379	41.46439	#1626°0-	ċ	154 (4326	17716.0	0.78405	7282.71-	-17,15245	73.57	107.03	. Sara	ESTEN'I	0.340)
(C, -C' (ii))	<i>C3</i>	がいっとい	c	-	0		1,05158	0.RBDH3	-15.19034		83.62	3K.3K	37.46	£1413	9800
C,(H)C, = C,H,C,	ຳ :	-1.13390	июсьть.			-153 67867	17716.0	19508.0	CT8801 21.	-16 69786	127,61	errs	38.24	0.77492	0.4916
$C_{\nu}(H)C_{\nu} = C_{\nu}H_{\nu}$	ť	O(1).1-	u	c	e	-132.74940	0.91771	0.15252	-15.93555	-15.76868	129.84	\$0.16	60.70	0.72040	0.5462
C,(C,)C, =C,H.C,	Ü	-1.13380	721/21/D	-0.73457	0	-154,19803	17716.0	0.78155	-17.40809	17.21783	126.39	19.65	56.95	0.80289	0.4637
(C'-C'0)	.0	-f.1,73HD	15PZLV	tsrct.o-	a	134.1980	177160	0,74155	-17,40869	(371 <u>C.</u> T).	8118	11911	17.79	1,81127	STARC 0
(C-C (I)) (C-C (I)) (C+C (I)) (C+C (II))	ນ້	BKLV	-0.9231R	c	. 0	sracts:	141140	0,87562	18647911-	-16.21864	07 19	112.60	31.36	1.7421	4718.0
$R(\zeta, H, -C, \zeta, H) = C$ $(C - C, \zeta, H)$	U	-1.13390	HICKER	c	•	-133 677066	17716.0	0.80561	-16 88873	16.69726	64.57	115.43	22.79	1.77684	0.34596
R,C,H, -C,(H)=C (C-C (i))	ئ	คายรอเล	40.9391R	o	С	\$0rLF151-	1,4419.0	0,81549	-16 (34)	.16,49325	65.50	1140)	30.58	1.76270	0.33183
$C - H \left(CH_1 \right) \left(t \right)$	J	-1.17PD	c	o	c	-152.74040	17110	0.83252	-15.95955	-15,76868	77.15	102.85	44.13	1,2353	0.18965
с. – н (сн.)		41,020,0-	U	=	٥	-152.54487	17716-0	0.86359	-13.73473	-13.56407	77.49	102.51	41.48	1,23564	Q. ISTOR
(" – H (tH ₁) (ii)	ن	-0.9291#	Alt20.tr	c	c	-153,47400	177190	0.RIS49	-16.69412	16,49325	4180	111.53	35.84	1.35494	0.29933
C - H (CH) (ii)	ر.	NICZGU-	HICEGO.	-0.92918	e	154,403,4	0.91771	0.77247	0117.11-	-17 41344	61.10	118.50	ינונ	1,4988	2003
H,C,C,H,CH, - (C - C (a))	نن	81626.0-	a	e	a	-152.544R7	0.91771	0.86339	-43.75493	-13.36407	53.82	116.18	30.08	1.83879	0.38106
H,C,C,H,CH, - (C - (* (a))	C.	-0.3291K	-0.9291×	c	e,	-153 47406	17116.01	675 18'0	-16,69413	-16.49325	56.41	133.59	20.24	1.90890	0.45117
$(R - H_3C, C, (H_3C, -R')HCH, -$ $(C - C, (\Phi))$	r,	-0.9291R	K1626'0*	#162G'U-	5	-154.402a	177160	Q.77247	-17.61330	17.42344	6,30	131.78	31.80	1,57162	0.51388
$(R - H_1C_2(R - H_2C_3)C_4(R^2 - H_2C_2)CH_1 - C_2(C_2)$	ر.	ж1626'0-	472457	ብ አንያን	-0.72457	-154,71860	0.91771	0.75889	-17.92860	977.71-	48.21	131.79	21.74	H20734	0.505.0
Iru(',C,(H,C,-H')HCH,-(C,-C',(d))	۲.	*(000)*	ж16269-	\$167G'D*	U	-154,40324	R.91771	0.77W7	-17.61330	-17,43244	48.30	51.20	21.90	1,97162	0.51388
$(R-C, (R-H_1C_s)C, (R-H_1C_s)CH_1 - (C-C, (e))$	ن	-0 72457	12457	47.7357	LSPRLO	6681517511	111160	0,76763	-17.97366	פתנו,ל).	70%	122.96	22.00	1,34462	X6267'U
$ienC_{\mathcal{L}_{i}}(H_{i}C_{i}-R^{i})HCH_{i}-$ $(C-C_{i}(0))$	٠٠٠	.0 72457	45.9291W	#16TG u-	ų	-154.19863	17716.0	0.78155	-17.40809	-17.21783	\$1.78	273	33	(1,924.1	611119
$\lim_{t\to t'} (R'-H_tC_s)C_*(R''-H_tC_t)CH_1 - IC_{-t'}(t)$	ئ	12157	13127.0	ינינויוי	18KL'u	-(\$4.\$1399	17716.0	0,76765	-17.92866	-17.7379	70.00	129.96	32.06	1.94462	0.49298

			The state of the s			-				r		⊱					5
i arain ciers] e [] ([C = C Group	() -(; (i) Greup	diago	(jii) Grand Grand	Group	Group	Group	(i)	Group Group	G deap	Graup	Group	Group .	Group	Group
	-	-	-1	-	-	-	2	_	_	2		1	-	-	-		-
	-	0	0	0	•	0	-	0	7	-	c	0	0	0	0	0	0
	•	e	0			۰	0		•	٥	٥	0	0	0	0	٥	٥
	9.5	2,0	9,5	2.0	20	50	0.75	0.75	0.75	0.75	0.75	0.5	5.0	0.5	0.5	50	0.5
	0.81317	71613.0	17116.0	-	-	-	-	-	-	-	_	-		-	1	-	-
	-	-	-	_	-	-	-	-	-	-	-	-	-	-	-	1	1
	-	-	171160	17716.0	0,91771	17710,0	17710.0	17716.0	17716.0	0.91771	17716.0	17716.0	17716.0	0.91771	17719.0	17716.0	17719,0
	-	0	0	_		-	-	-	0	-	-	0	0	0	-	-	٥
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	0.5	2.0	5.0	20	0.5	0.5	0.75	0.75	0.75	0.75	0.75	0.5	0.5	50	0.5	0.5	50
	0,81317	0.81317	0.91771	_	-	-	-	-	-	-	-	_	1		-	-	-
(-6:)	.3287721	-32.14474	-102,08992	-30,19634	-30.19634	-30.19634	-72,03387	-37.10024	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.101.12	-28.79214	-29.10112	-29.10112
l', (aF)	8.35160	8.21394	21.48386	9.50874	9.50874	9.50874	26.02344	13.17125	38.02728	25.78002	12.876\$0	9.33352	9,33352	6.37273	9.33352	6.37273	9.37273
7 (01/)	7,61688	7,32700	34.67062	7,37432	7,37432	7,37432	21.95990	11.58941	32.53914	21.06675	10.48582	6.77464	6,77464	6,90500	6,77464	6.90500	6,90500
1. (ef.)	г	-3.66350	-17,33531	-3 68716	-3.68716	-3.68716	-10.97995	-5.79470	-16.26957	-10,53337	-5.24291	-3.38732	-3,38732	-3.45250	-3,38732	-3.45250	-3.45350
E(m m) (cl.)	-14,63489	-14.63489	0	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
Minus In 18) (el')	-3,71674	-3.19677	0	٥	٥	. 0	0	-1.13379	0		0		0	0	c	0	0
E, Les m) (cl')	-10.91815	-10.97139	•	-14,63489	-14,63489	-14,63489	-14,63489	-13,50110	15,56407	-15.56407	-14.63489	-15.56407	.15.56407	-15,35946	-15.55407	-1535946	-15,35946
Eylmyou) (cV)	31,63531	-31,63541	-63.27075	-31.63534	-31.63534	-31.63534	-49.66437	-31.63539	-67,69451	49,66493	-31,63533	-31.63537	-31.63537	-37.63535	-31.63537	-31.63535	-31,63535
Er (alom - alom, negr', AO) (el')	-1,44915	-0.92918	-2.26759	-1,44915	-1,85836	-1.44915	0	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1,44915	-1,44915
E, (un) (eF)	-33,08452	-32.56455	-65.53833	-33.08452	-33,49373	-33 08452	-49.66493	-31,63537	-67,69450	-49.66493	-31.63537	-33.49373	-33,49373	-33,08452	-33.49373	-33.08452	-33,08452
a (10" rad/s)	8,31434	8.11389	43,0680	9,07851	16,4962	9,97851	15.2077	26.4826	24.9256	24.2751	24.1759	. 9.43699	9.43699	15,4846	9,43699	9.55643	9.55643
E, (el')	5.47264	5.34070	28,34813	6.56803	10.85807	6.56803	16.59214	17.43132	97807'91	15.97831	15.91299	621159	6.21159	10.19220	6,21159	6.29021	6.29021
E. (el')	-0.15312	-0.14888	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.26130	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
F. C. (el.)	0.08059	0.08059	0.17897	0.15895	0.09931	169931	0.35332 Eq. (13.458)	0.3532 Eq. (13,458)	0,35532 Eq. (13,458)	0,35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944	0.12312 [2]	0.12312 [2]	0.12312
E («!')	-0.11282	-0.10859	-0.15568	-0.08827	69891 0-	-0.11809	-0.07727	-0.08364	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Enc (eV)	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0,14803	0,14803	0.14803	0,14803	0.14803	0,14803	0.14803	0.14803	0.14803
Fylorent (eV)	-33.19734	-32.67314	-66.04969	-33,17279	-33,66242	-33.20260	-49.81948	-31,71901	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
Epoch (L. At sta) (CF)	-14,63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.53489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489
E (4, 10 '10) (et')	0	0	0	0	0	٥	-13.59844	-13.59844	-13.5%44	-13.59844	-13.59844	٥	۰	٥	٥	°	٥
" (c1)	3.77953	3,40336	7,51014	3,75498	4,39264	3.78480	7.83968	3,33765	12,49186	7,83016	3.32601	4.32754	4.29921	3.97398	4,17951	3.62128	3.91734

် ပို့ © င ن € ه ပ ပ | Table 15.55 | The total bond energities of transched-chain alternyl chlosides calculated writes be functional process commostline in the energies of Table 15.54 compared to the experimental values [2], | Franches | Fra

	εχυ. (2)	,	124 (ringl chloride)	(125.5 (Ving Cabardae) 123.8 (1.1-shehturosthyrkane)	(1,1-Schlorockýbra) 112.5 (rími chkride)			(1,334vvariese ChGcGo) 121,7 (1,334vvariese (2,437Go) (1,34svariese CC) (1,34svariese CC) (1,34svariese CC) (1,34svariese CC)		118.3 (2-neth; [propent]	(2-media/propere)	107 (propanc)	112 (prop.anc.) 113 8 (heaper) 110 8 (seebutanc.)	(hotane) (hotane) 111.4 (hothutane)				110.8 (sofmulane)		III.4 (lechume)	111.4 (isobiutane)	
		11691	121.55	813	5	118.36	113.84	97521	118.19	116.31	121.85	108 4H	110.49	110.49	309.50	1007*1	109.44	110.67	110,76	111,37	111.27	02,701
<u>÷</u> [0° D								13.46					'								
chin'un	ø. ©		11694	16,91					18.36		116.31				L	L						
IOM - GA	ø. ©								L				18.69	1569	_	35.05	25.0%			_		2.50
20. 2, 13 2, 0	(e, F;	0			н (256.0-	e	-1.R9R36	.1.8583ć		c		0		.•	-			-1.85R.W	a		-F.85836	
gre were us	V	1.00773			OKCISY	1,07647	0.81349			1.13mg		1,15796			1.15796			0.81549	1,04887	1.04887	1.04887	
reding an	ű.	67.0			-	4.75	-	.		52.0		n.75			3.75				0.75	27.0	a.75	
rom me pre	<u>ن</u> '	0.95310 (Cat (13 63))			0.8(317 (634 (15.11))	-	-	-		-		-			-			-	-	-	-	
arameters in	ਹ ਹ	a.75			-	67.0	-	-		-		-	,		-				0.75	87.0	27.0	
מ מיי וויכ מ	5- <u>[</u>	17710.0			0.86359	0.91771	64218.0	กรเชบ		-		-			-			ה, או גייני	0.91771	0.91771	a.91771	
atoulation	C and	009180			98129	0 K5251	0.81549	0 क्षेत्री		\$525×0		0.86359			0.86,150			0.81549	60278.0	20178D	QR7405	
values [1] In the c	Mon 2 Hybridization Desputies	C			5	-	7	**		=		п	÷		=			Ħ		_	-	
xpenmental	L'estante.	-12.30%4 C?			-12.96764 CJ	5755KH-	-16.64111 C,	-Incodel 1		=		Ξ			Ξ			- [0,6841] C.	-14.83575 C ₆	.14 R2513	-14,82573	
y chlondes and o	Attent Partification Designation	2				r	3			D.		7			٠			ĸ	•	5	~	
J-chain are	Įį.	.16,27430 (°,			-15.75493	-18,95954	-Incomi-	-اد بعادی		-15.95935		15.75.10.1			1875493			.) (',	.15.53013 C,	.(\$33033	.(15.5503) C.	
Dranche	(e)	1.54.19			\$ Inch	sters a	4206.2	4,75,79		34746		34233			3,4252			4.7958	4,1633	1633	4.795K	
melens o	, <u>a</u> [8,	3,356.25			13805	2.86175	2.16(175	2,46175 4,73,79		20457H		211106			107711			7K10.2	21173	11260-	2,90127	
angle para	'#]	1069JK			15052	21133	11/1/15	13331		2r457R		2.1710%			2 09711			291547	123164	1.91547	2,90327	
Table 13.56. The bond angle parameters of bitanched-thain attand chloride and experimental values [1]. In the calculation of 9, the parameters from the preceding angle were used. 2, is 5, follow - oken, angly AO.	Algebras to second	(0, -0.1	(C, -(1)	(C'-C1 (!) 7C'=C'()	(() () () () () () () () ()	(c;(H)c;=c;)	('.'(.')('.)'.) '.'.'.'.'	('.''.') ''.'.'.''	CHC.C.	$\mathcal{L}HC_{\mathcal{H}}H$	$(H^*C^* = C^*C^*H)$	Metridan LHC, H	לניניני	н'.5.)7	H. 142	₹,C,C,	H,7,7	ייי כ" כנ"כ"כ	#.'.'# #.'.'#	#'5'.# #'5'.#	س در" حداد رارد	7,5',5', 7,1',5',5'

ALCOHOLS
$$(C_n H_{2n+2} O_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl alcohols, $C_n H_{2n+2} O_m$, comprise an OH functional group and two types of C-O functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups (CH_3) at 5 each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The *OH* functional group was solved in the Hydroxyl Radical (*OH*) section. Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$. 15 shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \, eV$. To meet the equipotential condition of the union of the C-O H_2 -20 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the

$$c_2\left(C2sp^3HO\ to\ O\right) = \frac{E\left(O\right)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right) = \frac{-13.61806\ eV}{-14.63489\ eV}\left(0.91771\right) = 0.85395 \quad (15.114)$$

C - O-bond MO given by Eqs. (15.68) and (15.70) is

 $E_T \left(atom-atom, msp^3.AO \right)$ of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.65376 \, eV$ for the CH_3-OH C-O group. It is based on the energy match between the OH group and the $C2sp^3$ HO of a methyl group and is given by the linear combination of $-0.92918 \, eV$ (Eq. (14.513)) and $-0.72457 \, eV$ (Eq. (14.151)), respectively. For the alkyl C-O group, $E_T \left(atom-atom, msp^3.AO \right)$ is $-1.85836 \, eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each $E_D(Gimup)$ of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

									٠				
acie 13.37. The symbols of inneutonal groups of alkyl alcohols.	Group Symbol	HO	(i) O-U	C-0 (ii)	$C - H\left(CH_{j}\right)$	$C-H(CH_1)$	H)	(. – (; (a)	C-C(b)	(e) U-U	C-C (d)	(; – (, (e)	€) U=U
, auto 13.37. THE SYMBOLS OF	Functional Group	OH group	CH,OH C.O	Alkyl C-O	CH, group	CH, group	8	CC bond (n-C)	CC band (iso-C)	CC bond (tert-C)	CC (iso to iso-C)	CC (the t-C)	CC (1 to iso-C)

Table 15.58.	The geometrical bor	Table 15.58. The geometrical bond parameters of alky! alcohols and experimental values [1	il alcohols and expe	rimental values [1].								
Parameter	ОН Споир	C-O (i) Group	C - O (ii) Group	$C-H\left(CH_{s}\right)$ Group	$C-H\left(CH_{2}\right)$ Group	Group	C-C(a) Group	C-C (b) Group	(a) ン~ン	C-C (d) Group	C-C (c) Group	dnαnD Guanb
u (a ₀)	1.26430	1,79473	1.78255	1.64920		1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
$c'(u_{\flat})$	0.91808	1,33968	1,33512	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1,45164	1.45164
Bond Length $2c\cdot(A)$	0.971651	1.41785	1,41303	1.10974	1,11713	1.11827	1.54280	1.54280	1,53635	1.54280	1.53635	1.53635
Exp. Bond	176.0			1.107			1.532	1.532	1.532	1.532	1.532	1532
terest Ferest	(ethanol) 0.9451	1,4246 (methanol)	(ethanol)	(C - H propane) 1.117	_	t.122 (isobutane)	(propane) 1.531	(propane) 1.531	(propane) 1.531	(propane) 1.531	(propane) 1.531	(propane) 1.531
	(methanol)			(C-H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(butane)	(butane)
h,c (a _o)	0.86925	1.19429	1.18107	1.27295	1,29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
9	0.72615	0.74645	0.74900	0.63580	0.63159	500590	D 68600	0 68600	D ARRES	007870	086690	000000

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the state of the s					indicate of the control	11.	Course desiration on the section								
Bond	Atom	E,	E.	£7,	Ε,	Final Total	,	1,24	Ecutum	E(C2xn1)	.0	9	9	,	7
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2.p ²	(%)	(°)	(eV) Final	(eV) Final	•	· ©	. E	(°)	s" 🕃
н-оэ'н	0	-0.82688	۰	٥	•	64	1 00000	12698.0	1453431		07.511				
-H,C,O-H	0	-0 9291R	0	٥	۰		1.00000	0.86359	-15.75493		115.00	10.5	64.51	0.54405	0.37403
$H_1C = OH$ (C = 0 (i))	: 	-0.82688	0	0	0	-152.44257	17716.0	0.86923	-15.63263	-15,46177	65.96	83,41	\$6.30	1 21986	0.9988
H,C - OII (C - O (i))	0	-0.82688	•	0.	o		1.00000	0.86923	-15.65263		65.89	83.41	46.30	1.239%	0.09981
-H₁C, -OH (C:-O (ii))	, C,	\$1626'0-	91626.0-	0	۰	-153.47405	17716.0	0.81549	-16,68411	-16.49323	93.09	16'98	43.59	1.29114	0.04393
-+; c, -OH (C-O (ii))	0	-0.92918	0	0	o		1.00000	0.86359	-15.75493		02,79	82.80	46.50	1,22692	0.10820
c-+ (ch,)	ن	-0.92918	0	0		-152.54487	0.91771	0.86359	-13.73493	-13.56407	77.49	102.51	41.48	1 21564	0 18708
C-H (CH;)	Ü	-0.92918	-0.92918	0	0	-153.47405	0,91771	0.81549	-16.68412	-16,49325	68.47	111.53	15.84	32751	7,002.0
C-H (CH)	Ü	-0.92918	-0.92918	-0.92918	٥	-154.40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.50	11.17	1 47088	7
$H_3C_*C_*H_3C_*H_3$ – (C' – C' (a))	۲,	81626'0-	0	0.	0	-152.54487	17716.0	0.86359	-15.73493	-13.36407	63.82	116,18	30.08	1.83879	901810
H,C,C,H,CH, -	ť	81626.0-	-0.92918	0	٥	-153,47406	0.91771	0.81549	-16.68412	-16.49325	3641	171 50	76.05	8	
$R - H_3C_sC_s(H_3C_s - R)HCH_3 - C_sC_s(H_3C_s - R)$	Ü	-0.92918	-0.92918	81626.0-	•	-154,40324	171,60	0.77247	-17,61330	-17,42244	68.30	82.11	8 15	Control Control	illes o
$R - H_2C_s(R - H_2C_s)C_s(R - H_2C_s)CH_2 - (C - C_1(s))$	U	-0.92918	-0 72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866	-17.73779	482	131.73	27.12	7011/61	0.51388
$loc',C,(H,C,-R')HCH_1-$ (C'-C'(d))	ť	-0.92918	81626.0-	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	297762	O STRR
tent', $(R'-H_2C_s)C_s(R''-H_2C_s)CH_1-$ (C-C,(e))	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17,92866	-17.73779	\$0.04	129.96	22 66	1.94462	0.49298
ועיר: ָר', (H,C', - R') HC'H, - (C'-(' (ין))	υ.	-0,72457	-0.92918	-0.92918	٥	-154.19863	17716.0	0,78155	-17,40869	-17,21783	52.78	127.21	20.22	1.92443	0.47273
$ImC_{s}(R-H_{s}C_{s})C_{s}(R^{-}-H_{s}C_{s})CH_{s}-IC_{s}CC-C_{s}(D)$	ť	-0.72457	-0.72457	.0.72457	-0.72457	-154.51399	17716.0	0.76763	-17,92866	977.71-	20.05	129.96	3,6	00000	1000

Table 15.60. The energy parameters (eV) of functional groups of	rs (eV) of function	nal groups of alkyl	alkyl afcohols.									
Parameters	HO	() O-5	(ii) 0-3	ί.Η,	CH,	H-3	(a) U-U	(a) U-U	(:-(6)	(p) ::-::::::::::::::::::::::::::::::::::	(a)	ر-ر (ا
	Oronp	dioip display	Group	Granp	Group	dioip	this is	dinnip	dent	digit	dupio	diono
<i>n</i> ,	-	-		3	2	1	,	1	1 -	1	1	1
<i>'u'</i>	0	0	0	. 2	1	0	0	0	0	0	0	0
, n	0	0	0	0	0	0	0	0	0	0	0	0
· · ·	0.75	0.5	6.5	52.0	0.75	0,75	5.0	0.5	6.0	5.0	6.5	5.0
ر:	_	-	-	-	_	_	_	-	_	-	-	-
c,	0.75	-	1	1.	-	_	-	1	_	-	1-	-
5	_	0.85395	0.85395	17716,0	17716.0	0.91771	17716.0	17716.0	17716.0	17716.0	17716.0	17716.0
હે	-	٥	0	0	-	-	0	0	0	-	-	0
5	-	2	2	1	1	1	2	2	2	2	2	2
6,3	-	0	Q	3	2	-	0	0	0	0	0	0
	27.0	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
(.)"	_	1	1	-	1	-	_	-		_	-	_
V, (cV)	-40.92709	-33.47304	-33.78820	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	14.81988	10.15605	10.19068	38.92728	25.78002	12.87680	9.3332	9.33352	9.37273	9.33352	9.37273	9.37273
7 (aV)	16.18567	9.32537	9.47749	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (aV)	-8.09284	-4.66268	4.73874	-16.26957	-10.53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(. 11 10) (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15,56407	-15.35946	-15.35946
Δ1: n, m) (w) (wV)	0	-1.65376	-1,85836	o	0	0	0	0	o	٥	0	0
$E_T(w, m)$ (eV)	-13,6181	-12.98113	-12.77653	-15.56407	-15.56407	-14,63489	-15,56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$E_{\tau}(u_{s}, \omega)$ (aV)	-31.63247	-31.63544	-31.63529	-67,69451	-49.66493	-31,63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	-31.63535
$E_T(alom - alom, mxp', AO)$ (cV)	0	-1.65376	-1.85836	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
$E_r(\mu)$ (cV)	-31,63537	-33,28912	-33.49373	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (1015 rad 1.8)	44,1776	22,3978	12,2831	24.9286	1572.42	24.1759	9.43699	9.43699	15.4845	9.43699	9.55643	9.55643
\mathcal{L}_{K} (aV)	29.07844	14.74264	8.08494	16.40846	15.97831	15.91299	621129	6.21159	10.19220	6.21159	6.29021	6.29021
F. (cV)	-0.33749	-0.25287	-0.18841	-0.25352	-0.25017	996770-	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\widetilde{E}_{ m lim}$ (cV)	0,46311	0.12808 [19]	0.13328	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312 [2]	0.12312	0.12312 [2]
E (aV)	-0.10594	-0.18883	-0.12177	-0,22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eng (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803
Er (thurs) (UV)	-31.74130	-33.47795	-33.61550	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33,59732	-33.18712	-33,18712
Esery ly, so my (cV)	-13.6181	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Estand (r. do 180) (cV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
18,1 (am) (aV)	4.41035	4.20817	4.34572	12.49186	7.83016	3,32601	4.32754	4,29921	3.97398	4.17951	3.62128	3.91734

Color Colo	Formula Name $C = C = C = C = C = C = C = C = C = C $	HO	(E) (C)	(E) 0-3	CH,	CH_3	H)	C-C (a)	(P) C-C	(C-C)	(P) (J-)	(0)	0,0			
1	-	dieno	croip	Group		,						(e)	د - د ((Calculated Total Bond	Experimental Total Bond	Relative Error
1			, =				0	0	0	0	٥	0	c	21 1 (20)	Energy (eV)	
1			• •			- (0		0	0	0			33 40563	21.13	0.00097
1			> <		-	7	0	7	0	0		• c		33.40303	33.428	99000.0
No.		> <		7	0		7	0		·c		> 0	45.26353	45.584	0.00046	
1			> <			m	0	m	0	0		o c		45.72088	45.766	0.00098
10 10 10 10 10 10 10 10	7		- (_	7	_	_	٣	0				> 0	57.72103	57.736	0.00026
1	0		0 (_	7	_	-	0	. ~	• •	> <	5 6	0	57.87858	57.922	0.00074
1	20.	_	0	_	~	0	c			> 1	۰ د	0	0	57.79359	57.828	0.00050
1			c.	_		4) T	> 0	200	۰ د	0	0	58.15359	58.126	-0 000 dz
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1	<u>-</u>	_	c	-	. ~		- د		n (٥,	0	0	٥	69.95129	056.69	00000
1	7	-	0	_	. ~	۰ د	, ,	- «	، د	m .	0	0	0	70.31129	70.246	0000
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0 1 0 0 0 0 0 0 0 0		_	0	-	- ~	٦,	۰ د	^	0	0	0	0	0	27 02647	20.00	0.00
0 0 0 0 0 0 0 0 0 0		_			۷ -	٠,		'n	0	0	0	0		82 10200	95.036	170000
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106.459 118.521 130.676 154 984			0	_	7	13	_	4	۰.		> <	> (0	106.35183	106,358	0.00000
118.521 130.676 154.984			0	_	_	•	0	• •	٠.		۰ د	>	0	106.42439	106.459	0.00032
130.676		_	0	_	<u>-</u>	٥		• •	> <	> 0	5 (0	0	118,50953	118,521	0.00010
154 984		_	0	_	_	=	• =	`=	> <	> 0	0	0	0	130.66723	130.676	0 00007
		-	0	_		· <u>v</u>		= 5	۰ د	0	0	0	0	154.98263	154 984	10000

(C)	101.53 (methanot)	8 (cthandl)	7 (ethanol)	_	(Sobatare) (13.8 (Sobatare) (Sobatare) (Sobatare)	 				7 (rsoburane)		7 (isoburane)	111.4 (isoburane)
(3) (5)	NZ.701	106.78	110,17	108.44	110.49	110.49	109.50	109.44	109,44	110.67	110.76	111.27	111,27
				_									_
(e) (e) (e)					15.69	69.51		10.56	70.56				-
(e V)	0	0	-1,65376	0	59	99	0	11	π)	-1.85836	0	0	-1.85836
ᢐ	17716.0	17719.0	0,83472	1,15795			1.15796			0.81549	1.04687	1.04887	1.04887
₄	0.75	57.0	-	6.75			0,75			1	27.0	0.75	57.0
ບັ	-	-	-	-			-			-	-	1	-
ψ	0.75	0.75	~	-			_			-	0.75	0.75	0.75
C ₁	171160	0.91771	0.85395 (Eq (15.114))	ı			-			0.81549	17710.0	0.91771	17716.0
C ₁	-	-	0.81549	0 86359			0.86359			0.81549	0.87495	0.87495	0,87495
Atom 2 Hybridization Designation (Table 15.3.A)	_	-	٥	н			æ			22	-	-	_
Erostonic Atom 2	-14 82575	-14.82575	90819 CI-	π			Ξ			-16.68412 C.	-14.81575 C.	-14.82375 C,	-14.82575
Atom ! Hybrid ration Designation (Table 15.3.4)	_	_	×	7			7			25	\$	8	3
E-contract About 1	-14.82575	-14.82575	-16 68412	-15.75493			-15.75493			-16.68412 (',	.15,53033 (° <u>.</u>	-15.55033	-15 55033
2c' Terreltral Alones (a_a)	3.6697	3.6515	4.5826	3,4252			3.4252			4 7958	4 (633	4 1633	4 7958
2c' Ibnus (a,)	1.83616	1.83616	2.67024	2.11106		i	1 00211			291547	211323	1.007.1	2.90,27
2c' Doná i (q _a)	2,67935	2,67024	291547	2,11106			2.09711			2,91547	2.91547	291547	2,90327
Aleras of Angle	(C; -0 (I))	((i) O-'.)) HO'.)7	(C, -0 (ii))	Mohelima ZHC, H	בני לנילי	H1.5.77	H, 7H2	77.7.77	H*.5'.77	ַּרָהָי עניניני	4C,C,H	H*,5°,37	'.5'.5'.37

ETHERS $(C_n H_{2n+2} O_n, n = 2,3,4,5...\infty)$

The alkyl ethers, $C_n H_{2n+2} O_m$, comprise two types of C-O functional groups, one for methyl or t-butyl groups corresponding to the C and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups (CH_3) at each C end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO 15 and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the C2sp3 HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \, eV$. To meet the equipotential condition of the union of the C - O H_2 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the 20 C-O-bond MO given by Eq. (15.113) is $c_2(C2sp^3HO \text{ to } O) = 0.85395$. $E_r(atom-atom, msp^3.AO)$ of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.44915 \, eV$ for the $CH_3 - O -$ and $(CH_3)_3 \, C - O -$ C-O groups. It is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the $C2sp^3$ 25 HO of a methyl group as given by Eq. (14.151). For the alkyl C-O group, $E_r(atom-atom, msp^3.AO)$ is -1.65376 eV. It is based on the energy match between the O AO and the C2sp3 HO of a methylene group and is given by the linear combination of $-0.72457 \, eV$ (Eq. (14.151)) and $-0.92918 \, eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

alkyl ethers	Grotin Combo!	man da	(i) 0-2	C-0(ii)	(1) 11	(5,72)	(HU)H=0	(1,12)	C – H	C-C (a)	C – C (b)	(a) (j = 1)		(b) 2 - 2	(c) (c)
The symbols of functional groups of alkyl others	Functional Group	C-O (CH, -O- and (CH,) C-O-)		((mux))	CH ₃ group		dnorg run	CH	CC bond (n-C)	CC hond (iso.C)	(1) (1) (1) (1) (1) (1) (1) (1) (1) (1)	לבי החוות (נפוג-ר)	CC (iso to iso-C)	CC (t to t-C)	CC (t to iso-C)

		נו	Group		2.1072		1.4516		1.5363			1 532	(ocouou)	on adold	ונכיו	(butane)		1 53100	
	(3) (2)	3	dnes		2.10725		1.45164		1.53635			1.532	(propane)	123		(ontane)		1 50750	
	(g) C-C	2	dinoip		2.12499		1.45744		1.54280			1.532	(brobane)	1.531	(butane))	1	1.24616	
	(a) C-C	Group		2 1070	2.101.2	1 46164	#01C+:1		1.53635		-	766-1	(propane)	1.531	(butane)		1 52750	277	i
	(e)	crond		2.12499		1.45744		1 64380	1.34260		1 533	(annun)	1 53 1		(butane)		1.54616		
(a) <u>J-J</u>		d to to		2.12499		1.45744		1.54280			1.532	(propane)	1.531	(hutana)	(omeno)		9104		
C-H	Group		20,000	1.0/465	1000	1,0000		1.11827				1.122	(isobutane)			1,000	*7567	0.6300€	
$C-H(CH_{\star})$		7	1 67133	771/00	1.05563	Cocon.		1.11713		1.107	<i>H</i> ~3)	propane)	1117	(- H L L L	(o unane)	1.29569		0.63159	
C-# (CH,)	2		1.64920		1.04856			1.10974		1.107	H-0)	ргорапе)	(.117	(C-H butane)	1	1.27295	003670	0.63580	
ייים ליי	4000		1.79473		1.33968		,	1.41785			1.418	(ethyl methyl ether (avp))			1 10420	6746111	0.74645		
Group		1,80717		1 34431	I Charles		7,500	27		1 416	014.1	(dimethyl cther)			1.20776	200710	0.74388		
		00		(a')		DOUG	Length	2c' (A)		cap. bond	1000	£			0,c (a ₀)	,			

Table 15.65. The MO to HO intercept geometrical band parameters of alkyl ethers. R.R.R" are H or alkyl groups. Er, is Er, arom - atom. Intel'AO)	trical bond	parameters of al	kyl ethers. R, A	?.R" are H or :	ılkyl groups. 🗜	is Er (atom -	atom, msp'AO	<u>~</u>							
Bond	Atom	<i>E</i> , (eV)	(eV)	E,	Er (eV)	Final Total Energy	13	.13	Ecutor)	$E(C2xp^3)$:o ©	9.	9, 6	(a)	d. (a)
		Bond I	Bond 2	Bond 3	Bond 4	(eV)	(0,1)	(40)	Final	Final	()		3	(2)	(0_1)
C-H (OC. H.)		-0.724S7	6	٠		.152.34026	12216'0	0.87495	.15.55033	15,35946	. 28.17	101.15	42.40	11111	0,16921
H,C,-O-C,H, (CH,),C,-O-C,H, (CH,),C,-O-C,(CH,), (C-O (0))	ئ	-0.72457	0		o	7501-E151-	17710	0.87493	:15.55033	.15.35946	16.59	14.02	46.10	91622.1	0.09112
H.C., -0-C,H, (CH,),C,-0-C,H, (CH,),C,-0-C,(CH,), (C-0 (ii)	0	-0.73457	-0.71457	e	٥		1,6000	0.83600	-16.27490		72.66	¥5.78	43,74	1,30555	0.03\$76
$-H_{\mathcal{L}_{\alpha}} - \mathcal{O}_{\mathcal{L}_{\alpha}}(CH_{\alpha})_{\beta}$ $-H_{\mathcal{L}_{\alpha}} - \mathcal{O}_{\mathcal{L}_{\alpha}}H_{\beta}$ $(C - O \text{ (ii)})$	u'	.0,82688	-0,9291R		0	57175.831.	0,91771	0.82053	-(6.5RIRI	-16.39095	92.41	\$7.39	43,35	1,305.12	0,03456
$-H_1C_* - \mathcal{OC}_*(CH_j),$ $-H_1C_* - \mathcal{OC}_*H_j,$ $(C - O(ii))$	О	-0.72457	-0,RZGHR	v	0		1.0000	0,8307£	0527720		93.33	16.67	43.98	1,29138	0.04829
$-H_1C_a - O - H_1C_a - (C - O (ii))$	o	-0, K2688	-0.426kg	0	0		1,00000	0.12562	-16,47951		92.87	ET.13	99'£+	62862'1	0.04138
C-H (CH,)	Ü	.0,92918		G	•	-152.54487	0.91771	0,16359	-15,75493	-15.56407	77.49	10,251	19'17	1,23564	0.18708
C-H (CH ₂)	U	-0.92918	-0.92918		۰	-153,47406	17710.0	0.81549	-16.61412	-16,49325	68.47	111.53	35.84	135486	0.2933
(C-H (CH)	C	-0.92912	40.02018	#1626/D-	0	-154.40324	17719.0	0,77247	-17.61330	-17.42244	61.10	06.811	15.15	1142911	0.37326
H,C,C,H,CH, -	3	-0,929!X	o	ū	0	-152.54487	17710,0	0.86359	-15,75493	-15,56407	63.82	116,18	30.08	1.83879	0.38106
ונ-נ"אינא"- אינ"ג"אינא"-	5	-0.92918	#1626'0"	0	٥	-153,47406	17710.0	0,81549	-16.68412	-16.49325	56.41	123.59	26.06	1,90190	045117
$(R-H_2C_aC_a(H_2C_b-R^a)HCH_2-$	رد ا	-0.9291	#10Z0,0-	\$1626.0-	c	-154.40324	0.91771	0,77247	-17,61330	-17,42344	48.30	131.70	21.90	1.9716.1	0.513%
(C-C, (G))	ر.	\$1626°0-	-0,72457	15-21.0-	45427,0-	-154,71860	17716.0	0.75889	-17.92866	017.67.51.	48.31	67.161	21.74	bc78C.1	0.502.0
$loo(C_{i}C_{i}(H_{2}C_{i}-R))HCH_{1}-$ $\{(C-C_{i}(d))\}$	ڻ	81626.0-	.0.92918	-0,9291 2	0	-154,40324	17710.0	0.77247	-17.61330	-17,42264	48.30	131.70	21.90	29126'1	0,51388
(C-C'(2))	ر.	18447.0-	-0.72457	israru-	72857.0-	66215751*	14416.0	0.76765	-17.92866	-17.73779	\$0.0M	96.621	22.66	1.94462	0.49298
(C-C'(0))	1,5	-0.72457	*10 <u>2</u> 291#	x1676'17	ų	-(54,19863	17716.0	0.78155	-17.40869	-17.21713	\$2.78	22.12.1	10.04	1.92443	0.47279
$lac_{\bullet}(R-H;C_{\bullet})C_{\bullet}(R^{-}+I;C_{\bullet})CH_{\bullet}-$	ť	-0.72457	-0.72457	-0.72457	-0.724S7	-154.51399	177100	0,76765	-17.92866	•17,73779	\$0,04	129.96	99 22	1.94462	0.49298

The Live, the energy parameters of the control of t	S CV J DI RIHELION		CINCIA		n-,,	(a) ()=()	(A) () + ()	(- C (e)	C-C (d)	(i) (j - j)	ر-ر (ع
raranders	Group	Gramp	, min	, diam	Group	Group	Group	Group	Group	Group	Group
11	-	-	3	2	-	-	-	-	_	1	-
	•		2	-	o	0	0	0	0	0	0
	•	0	0	0	•	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	-	-	-	-	-	-		1	-	-	-
	-	-	_	_	-	-	-	-	-	1	-
	0.85395	0.85395	0.91771	17710,0	17716.0	17716.0	17110	0.91771	0.91771	17710	17719.0
	0	0	0	-	-	٥	0	0	-	1	0
3	7	2	_	_	-	7	7	2	2	2	2
	0	0	3	2	-	0	0	0	С	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	5.0	0.5	0.5	0.5	20
	-	I	_	-	-	-	_	-	-	1	_
P (cP)	-33.15757	-33.47304	-107,32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (aV)	10.12103	10,15605	38.92728	25.78002	12,87680	0,33352	9.33352	9.37273	9.33352	9,37273	9.37273
7 (aV)	9,17389	9.32537	32.53914	21,06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (aV)	-4.58695	4.66268	-16.26957	-10,53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.n m) (aV)	-14.63489	-14,63489	-15.56407	-15.56407	-14,63489	-15,56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
DE WAIN (to m) (eV)	-1.44915	-1.65376	0	0	0	0	0	0	0	0	٥
E. (m m) (el')	-13.18574	-12.98113	-15.56407	-15,36407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
12, n, vo) (cV)	-31,63533	-31,63544	-67,69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31,63537	-31.63535	-31.63535
E. (atom - atom, nixp', AO) (aV)	-1,44915	.1.65376	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (vo) (cV)	-33.08452	-33.28912	-67,69450	-49.66493	-31,63537	-33.49373	-33.49375	-33.08452	-33,49373	-33.08452	-33.08452
(10" rad/s)	12.0329	12,1583	24.9286	24,2751	24,1759	6,43699	9.43699	15.4846	9.43699	9.55643	9.55643
F. (eV)	7.92028	8.00277	16,40846	15.97831	15.91299	6.21159	6.21159	10,19220	6.21159	6.29021	6.29021
E, (aV)	-0.18420	-0.18631	-0.25552	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Extra (CV)	0.13663	0.16118	0,35532	0,35532	0.35532 (Eq.(13.458))	0,12512	0.17978	0.09944	0.12312 [2]	0.12312 [2]	0.12312
E. (c.V.)	-0.11589	-0.10572	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
(E. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803
Fy feman (41)	-33.20040	-33.39484	-67.92207	-49.80996	-31,70737	-33,59732	-35,49373	-33.24376	-33.59732	-33.18712	-33.18712
Example, so no! (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emple, so no! (cV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	
$E_{\mu}(\omega_{max})$ (cV)	3,95062	4,12506	12.49186	7,83016	3,32601	4.32754	4.29921	3.97398	4,17951	3.62128	3.91734

Tormuta	Name	(C)	(E) 0-0	Ć¥,		₩.)	(e)	ر - ر (۹)	((. (e)	C-C (d)	(-)	C-C (S	Calculated	Experimental	Relative
		5	a D D										Tetal Bond	Total Bond	Error
15	Principles of the Paris												Energy (4V)	Energy (eV)	
20	Directing cine	7 .	۰.	*	۰.	0	•	•	0	o	0	٥	32.84496	31,902	0.00174
2 2	Einyl metayl siner	- 4	- •	F4 1		0	_	0	0	0	•	0	45,19710	45.183	0.00030
2 6	A Code of the Code	5 .	٠, .	N	7	0	7	0	0	0	0	0	57.54924	57.500	-0.000\$6
2 0	Methyl propyi chizz			2		c ·	~	0	0	0	0	0	57,35480	57.355	0.0000
2 (Schropy mentyl enter	- 1	- 1	m. 1	0		•	7	0	0	0	0	57.45569	57.499	0.00075
2 0	Cipiopyi cilie	.	7 :	Α.	4	0	₹	0	0	0	0	0	81.86464	\$1.817	-0.00059
	a Britis of a factor	۰.	٠, .	4 .	э.	- 1 ·	0	•	o	0	0	0	82.06642	82.088	0,00026
2 0	Parties and a series			7 .	- (۰.		0	-	0	•	o	82.10276	82.033	-0,00085
2 0	Dibum about 1	- 4	- (0 1	٥,		0	~	~	0	0	٥	94.36135	94.438	0,00081
2 9	Diese Lind often	> 0	۷,	٧.	۰.		•	•	0	0	0	0	106.18004	106.122	-0 0005s
2 9	Die hay ates	·	9 6	٠.	N T	м (64 ·	4	•	0	0	0	106.38182	106.410	12000.0
9 9	r-Burd schund other	•	> -	٥,	٠.	٥.	0	0	•	٥	0	0	106,65628	106.425	-0.00218
	יייייייייייייייייייייייייייייייייייייי		-	n	-	-	5	_	_	c	c	•	104 40073	106.407	2

E, is Er (atom - atom, msp' At) the parameters from the preceding angle were used. Table 15.68. The bond angle parameters of alky/ others and experimental values [1], in the calculation of $heta_{r}$,

(chi, 100, 100)

107

(propare)

(112

(propare)

(113

(propare)

(114

(primare)

(1108)

(intro)

(intro)

(intro)

(intro)

(intro)

(intro) 111.9 (ethyl methyl ether) (dimethyl ether) . . l fü.R (Gobuune) 111.4 (isobatane) 111.4 (isobume) <u>a</u> . . . Ž 5. 10 K 109.44 110.67 110.76 11.27 111.27 107.50 . E e . 70.56 72.50 0, © 18.69 69.51 1.65376 -1.X5R36 -1,85836 -1,85836 ê ç. 0.78155 1.15796 D,X3472 0,77699 1.15736 0,815.49 ٠,٠٠ 1,04897 1,04887 1,04RR7 5.7 0.75 27.5 0.75 _ 0.73 0.75 0.73 0.83395 (Eq. (15.1141) (1,77699 0.81549 17716.0 17716.0 17716.0 0.78155 0.81549 0.R6339 0.77699 0.KG359 0,K1545 ٠, <u>١</u> 0.87495 0.87495 5 7 0 æ n P. Contractor -17.40x69 -13 61806 -17,51099 -16,68412 C_e -14,82575 C_e 14.8233 C. 1. 14.8233 C. C. Ŧ ñ Ţ ñ 23 ** F. Calenda Atem ! .17.51099 -16.684412 -15.75493 -16,68412 C. -15.55033 C. -15.55033 C. -15.55033 C. -15.55033 2c' Tembes Awar (a,) 3.4332 3,4252 4.4385 4,4721 4.5607 4.1633 4,1633 4.795# 2,68862 2.67935 \$862.9T 2.11106 2.09711 2.91547 2,90327 1177011 2,91547 2,11106 2,01547 2,91547 (a) [E.K. 1,91547 2,90327 $\begin{array}{c} \mathcal{L}', \mathcal{O}C, \\ \mathcal{L}', \mathcal{O}C, \\ \mathcal{C}', \mathcal{O}C, \\ \mathcal{O}', \mathcal{O}', \\ `.'.'.'z

PRIMARY AMINES $(C_n H_{2n+2+m} N_m, n=1,2,3,4,5...\infty)$

The primary amines, $C_nH_{2n+2+m}N_m$, comprise an NH_2 functional group and a C-N functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), 15 $C_{10} = 1.5$, and $c_1 = 0.75$. In primary amines, the $C2sp^3$ HO of the $C - NH_2$ -bond MO has an energy of $E(C,2sp^3) = -15.35946$ eV (Eq. (15.18) with s = 1 and Eqs. (15.19-15.20)) and the N AO has an energy of E(N) = -14.53414 eV. To meet the equipotential condition of the union of the N - H H₂-type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the N - H-bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627$$
 (15.115)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a 25 corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the

C-N H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO\ to\ N) = \frac{E(N)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140 \quad (15.116)$$

 $E_T(atom-atom,msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.44915\,eV$. It is based on the energy match between the N of the NH_2 group and the $C2sp^3$. HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups, $-0.72457\,eV$ (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Table 13.03. The Symbols of	functional groups of primary a
Functional Group	Group Symbol
NH ₂ group	NH_2
C-N	C-N
CH ₃ group	$C-H(CH_3)$
CH₂ group	$C-H(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Darameter 1111	-	2			-	(2) .)			5.00		
	Group	Gamp	Group	Growp	Group	Group	Group	Group	Group	Group Group	Group Group
a (o,)	1.28083	1.92682	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c, (a)	0.95506	1.38810	1.04856	1.05553	1.05661	1.45744	1,45744	1,45164	1.45744	1.45164	1.45164
Bond Length 2c' (A)	1.0103	1,46910	1.10974	1,11713	1.11827	1.54280	1.54280	1,53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.010 (methylaminc)	1.47] (methylamine)	1.107 (C-H propane) 1.117 (C-H bulane)	(C-H propend) (1.17 (1.17 (C-H butane)	1.122· (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butene)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (burane)
h.c (a.)	0.85345	1,33634	1.27295	129569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
น	0.74566	0.72041	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

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Table 15.71. The Mo	
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Table 15.71. The INO to the intercept geometrical bound parameters of primary and		י המשווניהים כי	=	ca. A, II, A care is at anyt groups, of is of anim - anim, my .AU.).	ednors strong		יאי – מינושיי שניא	÷							
Bond	Atom	£7.	15,	16,7	E _T	Final Total	1,1	'Ked	Economic	$E(C2sp^2)$.6	9	9	ď,	ď,
		(eV) Bond I	(eV) Bond 2	(eV) Band 3	(eV) Bond 4	(12xp)	(a.)	(°)	(eV) Final	(eV) Final	<u> </u>	©		(%)	(%)
H,CN(H)-H	λ.	-0.72457	0	0	0		0.93034	0.87495	-15.55033		00:811	62.00	8.33	0.54432	0.41075
$-H_1C_sN(H)-H$	2	-0,72457	0	0	0		0.93084	0.87495	-15,55033		118.00	62.00	28.23	0.54432	0.41073
H,C-NH,	ن	-0.72457	0	0	0	-152.34026	0.91771	0 87495	-15 55033	-15,35946	85.28	94.72	10.73	1,46010	0.07200
H,C - NH,	2	-0.72457	٥	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0,07200
-H,C, - NH,	ر.	-0.72457	-0.92918	0	0	-153.26945	17716.0	0.82562	-16.47951	-16 28854	80.20	98.80	37.50	1,52858	0.14048
-H,C, - NH,	>	-0.72457	٥	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0.07700
('-H (CH,)	i	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	1,23564	0.18708
$(C-H(CH_1))$	Ü	-0.92918	-0 92918	0	0	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	11.53	35.84	1,35486	0.29933
(H.) H)	t	-0.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17,61330	-17,42244	61.10	118.90	11.11	1.42988	92575.0
$H_sC_sC_sH_sCH_s-$ $(C-C_s(a))$	υ,	-0.92918	0	0	۰	.132.54487	0.91771	0.86359	15.75493	-15.56407	63.82	116.18	10.08	97818.1	901850
$H_1C_LC_RH_1CH_1-$ $(C-C_L(a))$	τ'	-0.92918	11626.0-	0	0	.153,47406	0.91771	081349	-16.68412	-16.49325	16,01	123.59	26.06	1.90290	0.45117
$R - H_i C_i C_i (H_i C_i - R^i) H C H_i - (C - C_i (b))$	ť	-0.92918	\$1676.0°	-0 92918	o	-154 40324	111160	0.77247	-17.61330	-17.42244	48.30	07.181	21.90	1,97162	0.51388
$(C - H_2C_*(R - H_2C_*)C_*(R^* - H_2C_*)CH_1 - (C - C_*(C))$	C,	91626:0-	-0.72457	-0.72457	-0.72457	-154,71860	177180	0.73889	-17,92866	-17.73	48.21	67.111	21.74	1,95734	0.50570
$i\omega C_{s}(H_{s}C_{s}-R)HCH_{s}-(C_{s}-C_{s}(d))$	C,	81526'0-	-0.92918	-0.92918	0	-154.40324	0.91771	ראנדדי.0	-17.61330	-17,42244	48.30	02.161	21.90	1,97162	0.51388
$(e^{-C_{s}}(R^{-} + H_{s}C_{s})C_{s}(R^{-} + H_{s}C_{s})CH_{s} - (C_{s}^{-} + C_{s}^{-})CH_{s})$	C ,	-0.72457	-0,72457	0.72457	-0.72457	-[54,51399	17716,0	0.76763	-17.92866	877.71.	50.04	129.96	22.66	1.94462	0.49298
$ICCC_{C}(H_{1}C_{r}-R^{r})HCH_{2}-ICCC_{C}(Q)$	7.2	-0.72457	-0.92918	-0.92918	Ġ	.154.19\$63	0,91771	0.78135	-17.40869	17,21783	52.78	27.72	20.22	1,92443	0.47279
$i\omega C_{\alpha}(R-H_{\alpha}C_{\alpha})C_{\alpha}(R^{-}-H_{\alpha}C_{\alpha})CH_{\alpha}-C_{\alpha}(C-C_{\alpha}(0))$	τ,	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17719.0	0,76765	-17.92866	977.ET.TI-	\$0.04	129.96	22.66	1.94462	0.49798

	HN.	γ-Ω Goup	C.H,		Group	Group	Granp Granp	Group	Group Group	Croup Croup	Group
п,	2	-	2	2	-	_	-	-	-	-	_
71,	0	0	2	-	0	0	0	· c	0	0	0
п,	~	0	0	0	0	0	0	0	اه	0	0
ر.'	0.75	0.5	0.75	0.75	0.75	5'0	0.5	0.5	5.0	0.5	0.5
	0.93613	-	_	-		_	1	1	1	1	1
6,	0.75	_	-	-	-	•	1	1	1	1	1
	0.94627	0.91140	. 12216.0	0.91771	17716.0	17716.0	177160	17716.0	17716.0	0.91771	17716.0
-5	0	٥	0	-	_	0	0	0	1	1	0
£,	-	2	_	-		2	2	2	2	7	2
6,4	2	0	3	2	-	0	0	0	0	0	0
	1.5	0.5	27.0	0.75	0.75	5.0	0.5	50	5.0	5.0	0.5
	_	-	-		_		_	-		1	1
V, (eV)	-77.89897	-32.46339	-107.32728	-70.41425	-35.12015	+1261.82-	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	28,49191	9.80175	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9.33352	9.37273	9.37273
T (uV)	30,40957	8,42409	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (aV)	-15.20478	-4.21204	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(*1 m) (cV)	-14.53414	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
Δί _{μισ} (** m) (cV)	0	-1.44915	0	0	0	0	0	0	0	0	0
Ey (m m) (0V)	-14.53414	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
E(1, 11 10) (4V)	-14.53414	0	0	0	0	0	0	0	0	0	0
Er (11,200) (cV)	-48.73642	-31.63534	-67,69451	-49.66493	-31.63533	-31,63537	-31.63537	-31,63535	-31.63537	-31.63535	-31.63535
Er (atom - atom, msp3,AO) (eV)	0	-1,44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
E, (w) (cV)	-48.73660	-33.08452	-67.69450	-49.66493	-31.63537	-33,49373	-33,49373	-33.08452	-33.49373	-33,08452	-33.08452
@ (1012 rad 1.x)	64.2189	18.9231	24.9286	24.2751	24.1759	9,43699	9.43699	15,4846	9.43699	9.55643	9.55643
E_{K} (eV)	42.27003	12.45552	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E. (eV)	-0.40690	-0.23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
\vec{E}_{km} (aV)	0.40929	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0,17978	0.09944	0.12312 [2]	0.12312 [2]	0.12312 [2]
E. (cV)	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eng (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803
Erfring) (cV)	-49.14112	-33,25079	-67.92207	-49.80996	-31.70737	-33,59732	-33,49373	-33.24376	-33,59732	-33.18712	-33.18712
E (4 10 10) (aV)	-14.53414	-14,63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E (V) (al o 10)	-13,59844	0	-13.59844	-13,59844	-13.59844	0	0	0	0	0	0
E. (tom) (cV)	7.41010	3,98101	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3,91734

Culculated Total Bond 23.88297 36.04067 48.19837 60.35607 60.78863 60.78863 (e) 2-2 Table 15.73. The total bond energies of primary amines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3].

Founds NH, C - N CH, CH, CH, CH, CH, CH, CH, C - C (a) C - C (b) C - C (c) C - C (d) C - C (d) C - C (d)

	1		7					_		_	,							
		<u> </u>		(methylamine	110.3 (methylamine	101.0 (methylamine) 107	(propane) 112 (propane) 113.8 (butane)	(isobutane)	(butane)	(isobutane)				110.8 (Isobujane)		111.4	(isobutone)	(isobutane)
	Cal. θ	<u> </u>		108.40	110.48	103.44	110.49		110,49	100.60	OC:601	109.44	109.44	110.67	110.76	,		111.27
	θ,	C																
	6	©																
	θ,	<u>ေ</u>					69.51		15.93			70.56	70.56					
ان	£,	(§		•	0	٥								-1.85836	0) in the second	-1.63830
atam, msp*. AO	٠٠			1.05679	0.97194	1.15796				1.15796				0.81549	1.04887	1.04887	5	200.
E, (atam -	ur			0.75	67.0	27.0				0.75				_	0.75	0.75		
used. E _r 18	ი.			-	-					-				-	-	-	-	
angle were	نة 			-	0.75	_				-				-	27.0	57.0	27.0	
the preceding	<u>ر</u> ا	T HIMY		-	0.88583	-			•	-				0,81549	17716.0	0.94771	0.91771	
rameters from	ر د ا		0.04637	Eq.(15.115))	0.91140 (Eq. (15.116))	0.86159				0.86359				0.81349	0.87495	0.87495	0.87495	
2c' 2c' 2c' 1: Atom 1 Atom	Hybridization	Designation Table 15 2 43	C.C.C. acou	=	z					H				25	-	-	-	
111 III C C C C C C C C C C C C C C C C	Ven 7			Ξ.	-15.35946	д		1		æ	-	†	-16 68413	ن	-14.82575 C.	-14,82575	-14.82575	;
Atom	Hybridization	Cestgrafion	,	2	5	7								ĸ	~	\$	~	
7/ I	0	Atem 1	130 72	*14.00.21-	-14.53414	-13,75493				-15,75493			-16.68412	٠,	-15.55033 C.	-15.55033	-15,55033 C.	•
2c'	Teminal	Aloms (a,)	7.00.	7.03	3.8816	3,4252				3,4252				4.7958	4.1633	4,1633	4.7958	
2¢'	7	(a,)	10101	2000	1.77620	3.11106				2.09711				2.91547	1,11323	11700.2	720327	
75.) Pared	(0)	110161		1.91013	2.11106				2.09711				2.91547	2.91547	2.91547	2.90327	
Alasteri Angle			HNH/		ZHNC."	Heliche ZHC,H	7,7°57,7°		H'D'.)77	Н. Н	7,5,57	H'.J'.)7	35.35.37	, H	£C, C, H	#'5'.37 ** C.	#1C	70,707

Table 15.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of $heta_{
m e}$, the parameters from t

SECONDARY AMINES $(C_n H_{2n+2+m} N_m, n=2,3,4,5...\infty)$

The secondary amines, $C_n H_{2n+2+m} N_m$, comprise an NH functional group and two types of C-N functional groups, one for the methyl group corresponding to the C of C-N and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may 5 comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino (NH) functional group was solved using the procedure given in the Hydrogen Nitride (NH) section. Using the results of Eqs. (13.245-13.316), the secondary 15 amino parameters in Eq. (15.52) are $n_1 = 1$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 0.75$, and $c_1 = 0.75$. In secondary amines, the $C2sp^3$ HO of the C-NH-bond MO has an energy of $E(C,2sp^3) = -15.56407 \, eV$ (Eqs. (14.514-14.516)); Eq. (15.29) with s=1 and s=2, Eq. (15.31), and Eqs. (15.19-15.20)) and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the N-H H_2 -20 type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 of Eq. (15.52) for the N-H-bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383$$
 (15.117)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the

C-N H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO to N) = 0.91140$.

As given in the Continuous-Chain Alkanes $(C_n H_{2n+2}, n=3,4,5...\infty)$ section, each methylene group forms two single bonds, and the energy of each $C2sp^3$ HO of each CH_2 group 5 alone is given by that in ethylene, $-1.13379 \ eV$ (Eq. (14.511)). In secondary amines, the N of the NH group also binds to two $C2sp^3$ HOs and the corresponding $E_T(atom-atom,msp^3.AO)$ of each C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379 \ eV$. It is based on the energy match between the N of the NH group to the two $C2sp^3$ HOs corresponding to the energy contributions to each of the two single bonds 10 that are equivalent to those of independent methylene groups, $-1.13379 \ eV$ (Eq. (14.511)), where the N-H bond is also energy matched to the C-N bonds. $E_T(atom-atom,msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is $-1.13379 \ eV$. It is based on the energy match between the N of the NH group to two $C2sp^3$ HOs corresponding to the energy contributions to the single bond that are equivalent 15 to those of methyl groups, $-0.72457 \ eV$ (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in 20 Tables 15.76, 15.77, and 15.78, respectively. As in the case of NH_2 (Eq. (13.339)), $C_{1o} = 2C_1$ rather than $C_{1o} = C_1$ in Eq. (15.52) for the C - N bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	NH
C-N (methyl)	C-N (i)
C-N (alkyl)	C-N (ii)
CH ₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H$ (CH_2)
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15,76.	Table 15,76. The geometrical bond parameters of secondary amines an	no parameters of seco	noally ainines and c	d experimental vatues 1	11,							
rammeter	Group	C-N (i) Group	C-N (ii) Group	$C - H (CH_3)$ Group	C - H (CH ₂) Group	dnou5 C—H	C - C (a) Group	C-C(b) Group	C-C(e) Group	C-C (d) Group	C-C (e) Group	C-C (f)
0 (20)	1.26224	1.94862	1.94862	1.64920		1.67465	2.12499	2.12499	2.10725	2.12499	2 10725	2 10726
c. (a)	0.94811	1,39593	1,39593	1.04856	1.05553	1.05661	1.45744	1,45744	1,45164	1 45744	1 45164	1.46164
Bond Length 2c' (A)	1.00343	1.47739	1.47739	1.10974	1,11713	1.11827	1,54280	1.54280	1.53635	1.54280	1.33635	1.53635
Fyn Rond				107	1,07							
Length	1.00 (dimethylamine)	1.455 (dimethylamine)		(C-H propane)		1.122 (isobutane)	1,532 (propane) 1,531	1.532 (propene) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane)	1.532 (propane)
				(C - H butane)	(C-H butane)		(butane)	(butane)	(butane)	(hutane)	(2001)	16.1
n.c. (0°)	0.83327	1.35960	1.35960	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1 \$4616	1 5750	Courane
υ	0.75113	0.71637	0.71637	0.63580	063150	A 63005	VVYOY	007070		D. Carteria	00136.1	UC/2C.1
						0,000,0	0.000.0	0.08000	0.08888	0 68600	000070	00000

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	Alon	7,7	F,	" " " " " " " " " " " " " " " " " " "	Er	Final Total	7,	7	Eran	E(C2so')	θ,	9	8	["	,	Г
		(eV) Bond I	(cV) Bond 2	(eV) Bond 3	(eV) Bond 4	CO279	(%)	(%)	(cV) Final	(eV)	ε	·©	E	(°)	s" (§°	
$H_3C_sN(C_sH_3)-H$	>	-0.56690	0.995 0-		,	6										_
-H.C.N(R.m.)-H	=	0.000	0 66600		,		0.53084	0.83232	-15.95954		118.18	61.82	5.20	0.54546	0.40264	Г
א כ – אא – כ ה	: :	0.30030	-0,30050	٥	٥		0,93084	0.85252	-15,95934.		118.18	61.82	\$	0.54546	0.40264	Т
יייי הייי הייי		-0.36690	0	О	0	-152.18259	14160	0.88392	-15.39265	-15.20178	84.14	95.86	20.30	303871	-	Т
n,c m - c.m,	>	-0.56690	-0.36690	0	0		0.93084	0.85252	-15.95954		80 95	\$0.00	7.		Zenson'n	_
-H,C, -NH -C,R	ان	-0.56690	-0.92918	0	0	153.11177	17716.0	0.83360	-16.32183	-16 13097	78 80	10.10	30.00	1.33008	0.13415	Т
-H,C, -NH -C,H, -	2	-0.56690	-0.56690	٥	۰		0.93084	0.85252	-15.95954		20.08	10.00	20.25	00000	0.16057	
C - H (CH,)	c	-0.92918	0	۰	۰	-152.54487	12210	088980	16 76 401	1		29.00	18.75	1.53908	0,13415	Т
C-H (CH,)	į.,	-0.92918	B10000		,				2000	13.30407	11.49	102.51	41.48	1,23564	0.18708	_
(n.) H (v.n)				,	7	-133.47400	0.91771	0.81549	-16.68412	-16.49325	68.47	11.53	35,84	1,35486	0.29933	
(m) / m	انا	-0.93918	-0.92918	-0.92918	°	-154,40324	17710	0.77247	-17,61330	-17,42244	61.10	118,90	31.37	1.42988	0.37326	_
$(C - C \cdot (a))$	نن	-0.92918	0	۰	· c	-152,54487	17719.0	0.86359	-15.75493	-13.56407	53.82	116.18	30,08	1.83879	0.38106	т-
H,C,C,H,CH,	್ 	81626'0-	+0.92918	۰	۰	-153.47406	17716.0	0.81549	-16.68412	-16.49325	24.8	23.69	20.50			
R-H,C,C, (H,C,-R')HCH,-	ļ.												80.17	0.80%.	0.45117	
(C-C (b))		-0.92918	-0.9291	-0.92918		-134,40324	17716.0	0.77247	-17.61330	-17.42344	48.30	131.70	21.90	1,97162	0.51318	_
$R - H_3C_s(R' - H_2C_s)C_s(R'' - H_2C_s)CH_3 - (C - C_1(0))$	ť	-0.92918	-0.72457	-0.72457	-0.72457	-154,71860	0.91771	0.75889	-17,92866	-17.73779	48.21	67.161	21.74	1.95734	0.50570	
$lsoC_sC_s(H_sC_s - R^s)HCH_s - (C - C_s(d))$	ئ	-0.92918	-0.92918	81626.0-	٥	-154,40324	0.91771	0.777.47	-17.61330	-17.42244	0.28	031.70	21.90	1,57162	0.5138\$	-,
$tertC_{r}(R'-H_{2}C_{r})C_{r}(R''-H_{1}C_{r})CH_{2}-(C'-C'(e))$	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154 51399	17716.0	0.76765	-17,92866	97.67.71.	20.08	129.96	2,66	1.94462	0.49298	
$(C-C, (H_2C, -R)HCH_1 - (C-C, (f))$	ڻ	-0.72457	-0.9291	\$1626'0-	9	-154,19863	0.91771	0.78155	-17.40869	-17,31783	52.78	127.22	24.04	1.9240	0,47279	
$lin(C_{*}(R-H_{*}C_{*})C_{*}(R^{*}-H_{*}C_{*})CH_{*}-$ $(C_{*}-C_{*}(0))$	ئن	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	47.73.77	50.04	129.96	27.66	1.94462	0.49298	
									1	_	-	-	_	_	_	_

Parameters	MM	(- N ()	(E) N - C	7.0	7.7	7.7	(5)	マープ	300	でして	(3) (-)	(a) (j-1)
	Group	Graup	Group	Group	Group Group	Group	Group	Group	Group	Group	Group	Growp
u'	1	1	1	3	2	_		1	-	-		-
\overline{u}_{i}	0	0	0	2	1	0	0	0	0	0	0	0
u_j	0	0	0	0	0	0	o	0	0	0	٥	0
[0.75	5.0	5.0	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
5	0.93613	1	1	1	-	_	-	-	_	-	_	-
c,	0.75	1	-	-	-	_		-	-	-	1	-
63	0.93383	0.91140	0,91140	0.91771	0.91771	0.91771	17716.0	171160	0.91771	17710	17719.0	17716.0
ς,	- 1	0	. 0	0	-		0	0	0	-	-	o
£,	_	2	2	1	_	_	. 2	2	2	2	2	2
¢,	-	0	0	3	2	_	0	0	0	0	0	0
ر!،	0.75	_	_	0.75	0.75	0.75	0.5	5'0	6.5	0.5	0.5	0.5
ζ,,	-	1	-	1	-	1	_	_	-	-	_	-
V, (aV)	-39.21967	-31.98456	-31.98456	-107,32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
V, (aV)	14.35050	9.74677	9.74677	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	9.37273
r(eV)	15.53581	8,20698	8.20698	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (aV.)	-7.76790	4.10349	4.10349	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3,45250	-3.38732	-3.45250	-3.45250
E(10 110) (cV)	-14.53414	-14.63489	-14 63489	-15,56407	-15.56407	-14,63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_{2,100}}(\omega_0 \omega_0)$ (aV)	0	-1.13379	-1.13379	0	0	0	0	0	0	0	0	0
E. [.w 110] (eV)	-14,53414	-13,50110	-13.50110	-15.56407	-15,56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
6, (n, and (aV)	-31.63541	-31.63540	-31.63540	-67.69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31.63535
$E_r\left(atum - atum, msp^3, AO\right)$ (eV)	0	-1,13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
Er (sm) (eV)	-31.63537	-32.76916	-32.76916	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10" rad / s)	47.06%	15.1983	26.0778	24.9286	24.2751	24.1759	9,43699	9,43699	15,4846	9.43699	9.55643	9.55643
Er (uV)	30.98202	10,00377	17,16484	16.40846	15.97831	15.91299	6.21159	6,21159	10,19220	6.21159	6.29021	6.29021
E, (uV)	-0.34836	-0.20505	-0.26859	-0.25352	-0.25017	-0.24966	-0.16815	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Fra (aV)	0.40696 [24]	0.12944 [23]	0.11159	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12317	0.12312	0.12312
E (cV)	-0.14488	-0.14033	-0.21280	-0,22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eng (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E, (imm) (cV)	-31.78025	-32.90949	-32.98196	-67.92207	-49.80996	-31.70737	-33,59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emma (1, 10, 111) (cV)	-14.53414	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
5 (V) (a. 1) (a.V)	-13.59844	٥	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
Entirmo (cV)	3.50582	3.63971	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

9. The fotal bond Nan Dimeliylamine Diethylamine Distropylamine Dispropylamine Dispropylamine Dispropylamine Dispropylamine	neergies of secondary amines coloulated using the Group Group 1 2 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	### Company Co	CH ₂	es of Table 15.78 cd. C.+C. C.H. C.+C. C.H. C.+C. C.H. C.+C. C.H. C.+C. C.H. C.H	(a) C-((b) (1-C)	(c) C~C	(g)	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	(f) Calculated Front Bond Energy (eV) 33 76895 60.22930 84.54.70 84.54.70 84.54.70 103.56010	Experimental	Action Error -0.00012 -0.00016 -0.00016 -0.00016 -0.00016
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	Cal. B	٥	<u> </u>		111.76	107.27		111.89	108.44		110.49		110.49		109.50	109,44	109,44	110.67	7, 91		111.27		7
	9	્	2																				
	9	્	2				1																
	θ,	· ©	<u> </u>	1			1			1	69.31		69.51			70.56	70.56						
÷	E,	(eV)			5	•		-1.8336	0						0			-1,85836	0		0	-1.85836	
- deim, moin -	ۍ.			27.10	00,100	0.95917		0.79816	1.15796						1.13796			0.81549	1.04887		1.04887	1.04887	
er (mom	ď		•	37.0		0.75		-	0.75						0.75			-	0.75		£.	0.75	
1 T 13	ن			-	•	-		-	: 		-				-			-	-		_	_	_
	ت			87.0		6.73	-	-	-						-	1		_	0.75		0.75	27.0	
	<u>.</u>	Albui 2		0.93383	Eq. (15.117))	0.87418	A1807.0		-						-			0.81549	0.91771		0.91//1	0.91771	
	٠.	- Magk		17716.0	0.91)40	(Eq.	91862 0		0.86339					0.000	6660			0.81549	0.87495	307.00	0.0 /493	0.87495	
nimed Aught 2c' 2c' 2c' 2c' 2c' C Aliam C Aliam C Aliam C Alian C C C C C C C C C C C C C C C C C C C	Hybridization	Designation	(Table 15.3.A)	_		z	82		×					2	:			ដ	-	-	-	-	
	Cristiania.			-14.53414	-15.56407	(E.117)	-17.04640		×		•			=			-16.68412	ر,	-14.82375 C,	-14.82575	ن.ٰ	-14.82575 C,	†
Atom	Hybridization	Designation	(Table 15.3.4)	z			29		7				_	,				4		,		٠	
	,	5 W	Alem t	-14.82575		-14.53414	-17.04640		-15.75493					-15.75493			-16.68412	۳	-15.55033 C.	-15.55033	-		
1,2,0	F	(0)		4.0661		3.8123	4.6260		3.4252					3.4252			200.7	0000	4,1633	4,1633		4.7958	
2c.	[hmd2 (a,)			2 79186	,	4.72186	2.79186		2.11106					2.09711			2.91547		2.11323	2,09711	1	2.90327	<u></u>
20,	United (((D _B))	•		2.09711	10,00	17069-1	2,79186		2.11106					1.09711			2,91547		2.91547	2.91547		2,903,27	
Alaims of Auglic			10000	(C-N (i)& (ii))	ZHINC.	(C-N (I) & (ii))	(C-N (i) & (ii)	McDit lens	н". Ж		ZC,C,C,		H,2,32	Makil ZHC, H	ZC.C.C.	4C,C,H	לכנ'כ'	is C.	LC,C,H 100 C,	H''S'37	70.00	, J. 151	ZC.C.C.

TERTIARY AMINES $(C_n H_{2n+3} N, n = 3,4,5...\infty)$

The tertiary amines, $C_nH_{2n+3}N$, have three C-N bonds to methyl or alkyl groups wherein C-N comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise 5 methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2CH)$ and t-butyl $((CH_3)_3C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In tertiary amines, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the N AO has an energy of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the C-N H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO to N) = 0.91140$.

As given in the Continuous-Chain Alkanes $(C_n H_{2n+2}, n=3,4,5...\infty)$ section, the energy of each $C2sp^3$ HO must be a linear combination of that of the CH_3 and CH_2 groups that serve as basis elements. Each CH_3 forms one C-C bond, and each CH_2 group forms two. Thus, the energy of each $C2sp^3$ HO of each CH_3 and CH_2 group alone is given by that in ethane, -0.72457~eV (Eq. (14.151)), and ethylene, -1.13379~eV (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy $E_{T_{ndaws}}\left(C-C,2sp^3\right)$ given as a linear combination of these basis elements is -0.92918~eV (Eq. (14.513)). In tertiary amines, the N binds to three $C2sp^3$ HOs and the corresponding $E_T\left(atom-atom, msp^3.AO\right)$ of each C-N-bond MO in Eq. (15.52) due to the charge donation

from the C and N atoms to the MO is $-0.92918 \, eV$. It comprises a linear combination of the energy for a primary amine, $-0.72457 \, eV$ and a secondary amine, $-1.13379 \, eV$.

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 5 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

1.

Table 15.81. The symbols of	Table 15.81. The symbols of functional proups of terriary amines
Functional Group	Group Symbol
20	V-V
CH, group	$C - H \left(CH_3 \right)$
CH ₃ group	C-H (CH.)
£	
CC bond (n-C)	(6) (7)
CC band (iso-C)	(a) (
CC bond (text-C)	(S)
CC (iso to iso-C)	(P) () -: ()
(2-1 01 2)	(i) (i)
CC (t to iso-C)	€ • • •

Ĺ	Parameter C-N (())	1 1								
	Group	Group	C-H (CH;)	Group Group	(: -(; (a) Group	ر -در (و) در-در (و)	(3) .) -:)	ر-(رو)	(a) 2-2	(J) J-J
	196313	1,64030					dinab	dnous	Group	Group
		12/40.1	1.07122	1.67465	2.12499	2.12499	2 10725	217600		
	1.40112	1.04856	1.05553	1.05661	1 45747	1	2,101.2	2.1499	2.10725	2.10725
					p#/C#1	1.43/44	1.45164	1.45744	1,45164	1.45164
	1.48288	1,10974	1.11713	(,11827	1.54280	1.54280	1,53635	1.54280	1,53635	1.53635
		1.107	1,107		1 637					
	1.458 (trimethylamine)	(C - H propanc)	(C-H propane)	1.132 (isobutane)	(propane)	(propane)	(propane)	I. S32 (propane)	1.532 (propæne)	1.532
		(C-H butane)	(C-H butane)		(butane)	(huttone)		1.53	1.531	1531
	1.37505	1,27295	1,29569	1.29924	1 54616	2000	(Olumbe)	(Dutane)	(butanc)	(butane)
	0.71372	0.63580	0.63159	0.63095	DIONE	1,34010	1.52750	1.54616	1.52750	1.52750
					200000	0.08000	0.68888	0.68600	0.68888	0.68888

and the state of t	Petition contra	to barameters of	tertiary ammes.	עיעיע קוב וו	or any a groups	. Cr 15 Er (and	dem, moro – mi									
Bond	Atom	ET	Er	£,	Er	Final Total	, ,	7,5	Ecutua	16(0) 84	.6	8	8	6	,	
		Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C.2 of	(°)	(°)	(eV) Final	(ev) Final	E	· (C)	E	(%)	, (g)	
$N-(C_aH_s),$	٠,	-0.46459		•	-	-152.08028	17716.0	0.88983	-15.29034	-15,09948	83.77	96.63	0007	1 50181	0 10371	
N (C, H,),	2	-0.46459	-0.46459	-0,46459	٥		0.93084	0.83885	-16.21933		78.02	101.98	36.64	1 57575	17413	_
$N - (C_aH_2 -)_3$	ζ,	-0.46459	11626'0-	•		-153.00946	17719.0	0.83885	-16.21953	-16.02866	78.02	101.98	16.64	1 57525	0 17413	
$N-(C_{\mu}H_{2}-)_{3}$	N	-0.46459	-0.46459	-0.46459	٥		0.93084	0.83885	-16.21953		78.02	86 101	36.64	1000	0.17413	_
$C-H(CH_s)$	ن	-0,92918			٥	-152,54487	1,416.0	0,86359	-15.75493	-15.56407	77.49	102.51	41.48	123564	0.18708	
C-H (CH,)	ن	-0.92918	.0,92918	٥	٥	-153,47406	17716.0	0.81549	-16.68412	-16.49325	68.47	11.53	35.84	1 15486	0.70011	
C-H (CH)	į	40.92918	.0.92918	1626.0-	°	-154.40324	0.91771	0.77247	-17,61330	-17,42244	61.10	118 90	11.17	1 47058	7.11.0	
$H_i(C_i,H_iCH_i - (C_i - C_i))$	U ¹	-0.92918	0	0	۰	-152,54487	0.91771	0.86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106	
$H_iC_iC_iH_iCH_1 - (C - C_i(a))$	ť	-0.92918	•0.92918	0	0	-153,47406	17712.0	0.81549	-16.68412	-16.49325	\$6.41	123.59	26.06	0.90820	0.45117	
$(R-H_2C_s(H_2C_s-R)HCH_2-(C-C'(b))$	υ	-0.92918	.0.92918	-0.92918	۰	-154.40324	17116.0	0.77347	-17,61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388	
$R - H_2 \mathcal{L}_1(R^- + H_2 \mathcal{L}_2)C_1(R^- + H_2 \mathcal{L}_2)C_2H_2 - (C - C C)$	ن	81626'0-	-0 72457	-0.72457	-0.72457	154.71860	17716.0	0,75889	-17.92366	-17,73779	48.21	131,79	21.74	1.95734	0.50570	
$lsmC_sC_s(H_sC_s-R^s)HCH_2 (C-C^s(d))$	ن	-0.92918	-0.92918	-0,9291	۰	-154.40324	17716.0	CASTT.0	-17.61330	-17,42244	0E 84	131.70	21.90	1.97162	0.51388	
$ter(C_{s}(R^{-}H_{s}C_{s})C_{s}(R^{-}H_{s}C_{s})CH_{s}^{-}-(C^{-}C^{-}(e))$	C,	-0,72457	-0.72457	-0.72457	-0.72457	-134,51399	17716.0	0.76765	-17.92866	erter.71.	\$0.04	129.96	22.68	1.94462	0.49298	
ler(C,C,(H,C,-R)HCH,-C,C,C,C,C)	50	-0.72457	81626.0-	81626'0-	占	.154.19863	17716.0	0.78155	-17.40869	17.21713	52.78	17.71	24.04	1.92443	0.47279	
$I_{XX}(R'-H_2C_s)C_s(R'-H_3C_s)CH_2-$	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.75765	-17.92866	ert67.71-	20.02	120,96	22.66	1.94462	0.49298	

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines. R,R,R are H or alkyl groups. E, is $E_*(atom-atom,n)$

Parameters	C~N Group	Group	CH, Group	droup Choup	Group	C-C(b) Group	C-C (c) Growp	Group	(e) Clade	C-C(f) Group
u)	_	3	2	-	-	-	-	-	-	-
n,	0	2	_	0	o	0	c	0	0	0
n,	0	0	0	0.	0	0	0	0	0	0
Ċ.	5'0	0.75	0.75	0.75	5.0	0.5	0.5	0.5	0.5	0.5
ر،	1	-	_	_	-	_	-	-	-	-
-61	1	1	1	1	1	-	-	-	-	-
د،	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	12216'0	17716.0	17716.0
c,	0	0	-		0	٥	0		1	0
د'	2	1	1	1	2	2	2	2	2	2
Ç,	0	3	2	1	0	0	0	0	0	٥
,	0.5	0.75	0.75	0.75	6.5	5.0	0.5	0.5	0.5	2,0
77.	1	1	1	1	1	-	-	l	_	-
V, (cV)	-31.67393	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.101.12	-28.79214	-29.10112	-29.10112
V_{μ} (eV)	9.71067	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (aV)	8.06719	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (cV)	-4.03359	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3,45250	25785.6-	-3.45250	-3.45250
E(.n no) (aV)	-14.63489	-15.56407	-15.56407	-14,63489	-15.56407	-13.56407	-15,35946	-15.56407	-15.35946	-15.35946
$\Delta \mathcal{E}_{u_1,u_2}(m,u_2)$ (cV)	-0.92918	0	0	0	0	0	0	0	0	0
$E_{\rm r}(\omega m)$ (eV)	-13.70571	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
$E_r(n,\omega)$ (eV)	-31,63537	-67.69451	49.66493	-31,63533	-31,63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r\left(atom - atom, msp^3, AO\right)$ (eV)	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
Er (sm) (cV)	-32,56455	-67.69450	-49,66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
w (10" rod / s)	18.1298	24.9286	24.2751	24.1759	9.43699	9.43699	15,4846	9.43699	9.55643	9.55643
$\mathcal{E}_{K}\left(vV ight)$	11.93333	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
\vec{E}_{o} (cV)	-0.22255	-0.25352	-0.25017	-0.24966	\$1891.0-	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exm (cV)	0.12944	0.35537 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	2) EZ) [2]	0.17978	0.09944	0.12312	0.12312	0.12312
ξ _m (eV)	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (aV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803
E_r (times) (vV)	-32.72238	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emus (c, 17 11) (cV)	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489
Emmy (c. 10 10) (cV)	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
Entirmy (cV)	3.45260	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4,17951	3 62128	3.91734

Table 15.85. The total bond energies of tertiary anvines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula Name C-N C+N C+N C+N C+N C+N C+C (a) C+C (b) C+C (c) C+C (d) C+C (e) C+C (f) C+C (f)

						_	_						
	Ехр. <i>в</i>	110.9 (tri methylamine	107 (dimethylamine) 107	(propane) 112 (propane) 113.8 (buzane) 110.8 (isohuine)	111.0 (Butane) 111.4	2			110.8	(Southwell)	111.4	(isobutane)	(isobutane)
	(Sal. 6	110,41	108.44	110.49	110.49	109.50	109.44	109,44	110,67	110.76	111.27	111.27	
	e. ©										\top		
	e .												
	θ • •			69.51	15.69		70,56	70.56					1
	E _r (eV)	-1.85836	0			o			-1.85836	0		-1.85836	
ישה האיווים	ď	0.79340	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
ר מושוו – מו	. v	-	0.75			0.75			-	0.75	0.75	0.75	
27 12 2	౮	_	-			-				-	-	-	
aen arama	<u>ن</u>	_	_			-			-	0.75	6.75	6.73	
9	C ₃	0,79140	-			-			0.81549	17716.0	17716.0	17110	
	م ا	0.79340	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Atom 2	Hybridization Designation (Table 15.3.A)	9	н			×			. 22	-	-	-	
Ļ	Alem 2	-17,14871	x			×	1	2,700	رن ا	-14.83575 C,	-14.82575 C.	-14.82575 C.	
) drank	Hybridization Designation (Table 15.3.A)	-	,			7			a		•	5	
1	Community Of Li Aloni I	-17.14871	-15.73493			-15.75493		-16 68472	ς,	-15.55033 C.	-15.55033 C.	-15.55033 C,	
2c'	Ternital Atems (a,)	4,6043	3.4252			3.4252			4.7958	4,1633	4.1633	4.7958	
76.	Bom12 (a,)	280224	2 15106			1.09711			2.91547	מנווג	2.09711	1.90127	
2c.	Demail (a _n)	2.80224	2.11106			20971		Ī	291547	2.91547	2,91547	2.90327	
Aben Angel 2c' 2c' 2c' 7; Ahren Angel 2c' 2c' 2c' 7; Ahren Angel 2c'		ZCNC	AHC, H	'כנ"כנ"כ	H*5°J7	H, 7H2	H,0,07	ZC,C,C,	in C.	ZC,C,H in C,	∠C,C,H ™ C,	2C,C,C,	ZC,C,C,

Table 15.86. The bond angle parameters of tertiary

ALDEHYDES $(C_n H_{2n} O, n = 1, 2, 3, 4, 5...\infty)$

The alkyl aldehydes, $C_n H_{2n}O$, each have a HC = O moiety that comprises a C = O functional group and a CH functional group. The single bond of carbon to the carbonyl carbon atom, C - C(O)H, is a functional group. In addition to the C = O functional group, formaldehyde comprises a CH_2 functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C - C bonds can be identified. The n-alkane C - C bond is the same as that of straight-chain alkanes. In addition, the C - C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C - C bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that E_{mag} is not subtracted since unpaired electrons are not created with fragmentation of the CH functional group of aldehydes. The CH_2 functional group of formaldehyde is solved in the Dihydrogen Carbide (CH_2) section except that the energy of each C-H MO is matched to the initial energy of the $C2sp^3$ HO (Eq. (15.25)). The C=O and C-C(O)H groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \, eV$. To meet the equipotential condition of the union of the C=O H₂-type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO to O) = 0.85395$. The unpaired electrons created by bond breakage of the double C=O bond requires that two times

the O2p AO magnetic energy E_{mog} (Eq. (15.60)) be subtracted from the total energy to give $E_{D}(Group)$ (eV) for C = O.

 $E_T(atom-atom, msp^3.AO)$ of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -2.69893~eV which is an energy minimum for 5 the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, -1.13379~eV (Eq. (14.247)), and a triple bond, -1.56513~eV (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the C-H bond in addition to the pair involved directly in the double bond with O. 10 $E_T(atom-atom, msp^3.AO)$ of the C-C(O)H group is equivalent to that of an alkane, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the aldehyde. In order to match energy between the groups bonded to the C=O, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing, $C_{1o}=2C_1$ rather than $C_{1o}=C_1$ in Eq. (15.52) for 15 the C-C(O)H bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each $E_D(corrup)$ of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.

Table 15.87. The symbols of functional groups of alkyl aldehydes.

	Groups of anyl and
Functional Group	Group Symbol
CH ₂ (formaldehyde) group	$C-H$ (CH_2) (i)
CH (aldehyde) group	CH (i)
C=O	C = O(i)
C-C(O)H	C-C(O)H
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ (alkyl) group	$C - H\left(CH_2\right)$ (ii)
CH (alkyl)	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

⊢	C(O)H C-H (CH)	C(O)H C-H (CH)	C(0)H C - H (CH)	⊢	}	(101)	0 - H (i)	(3) (1)	12 0	c c			
Group Group Group	Group Group Group	Group Group	Group			(E)	Granb	Group Group	Group	Group	Group Group	C-C (e) Group	C-C (f) Group
1.64010 1.67465 1.29907 2.04740 1.64000	1.29907 2.04740	2.04740		1 64920	ſ	1,6317							
						777.0.1	1.07403	2.12499	2.12499	2.10725	2.12499	2.10725	2,10725
	1.13977 1.43087	1.43087		1.04856		1.05553	1.05661	1.45744	1.45744	1 45164	77637		
										10161	1.43/44	1,45164	1.45164
1.10668 1.11827 1.20628 1.51437 1.10974	1,20628 1,51437	1.51437		1.10974		1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
1.208	1.208		1 102	1 107	_	701							
(acetaldeflyds)	(acctaldchyde) (formaldshyde) 1.315 (acctaldchyde) 1.310	1.515 (acetaldelyde	(acetaldelyde) (C-H propane)	(C - H propane)		7-0	1.122 (dephysons)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)	1.532 (propane)
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1.26354 1.29924 0.62331 1.46439 1.27304	0.62331 1.46439	46439	H	1 27704	٠	0,300.1		umane	(butane)	(butane)	(Instance)	(butana)	(butane)
+	100000	10000	+	200		1,27309	1.29924	1.54616	1.54616	1.52750	1.54616	1 \$7.50	1 63760
6,600.0	0.07.27	0.69887		0.63580		0.63159	0 63095	007870	00000			00.000	00175.1
								2000					

Table 18.89. The MO to HO intercept geometrical band parameters of alkyl aldehydes. R.R.R.R" are H or alkyl groups. E, is E, (alnm-atom, assp. AO).

Sond

2000	4														
	E 01	<u>,</u>	Ę,	E.	F.	Final Total			E	10.00	ė	G			
		(eV) Bond I	(eV) Bond 2	(cV) Bond 3	(cV) Bond 4	Energy (2sp*	(8)	િ	(eV) Final	(ev)	. C	· ①	s" ©	(g ²) (c	'è 'è'
HC.(0) - H (Cn) G)	1					(eV)				Final			:	:	:
(n) (cus) m - (cus) m		-1.34946	0	•	۰	-152.96515	17716.0	0,84115	.16.17521	14 09414	: ;;				
$-C_{*}H_{*}C_{*}(O) - H_{*}(CH_{*})(0)$	ن.	-L.Susus	-0.9291K	٥		-153 KWILL	121.00	77.00				17.00	40.18	123314	0,20748
H,C=0	9	1.34946	e					GHCKI'D	-17,10440	-(6.91353	64.93	115.05	33.69	1.39345	0.33684
-C,H,C,(H)=0	9	-1.34946		,	,		00000	0,84115	-16,[752]		137.27	42.73	66.31	0.52193	0.61784
RH,C, -C,(H)(O)	ن	1.34946	81040 G		, ,		1,00000	0 84115	-16.17521		127.27	42.73	16.99	0.52193	0.61784
H,C, -C,(HXO)	ار	-0.92918		, ,	3 4	-153.89434	144160	0.79546	-17,10440	-16.91353	135,34	44.66	87.63	0.57401	0.56576
-C,H; -C,(H)(O)		B1026 G	#10000 t/*			-1525467	0.91776	0 \$6359	-15,75493	-15.36407	72.27	£7.701	¥.17	1,69388	0.26301
C-H (CH.)		a later		,	٥	-153.47408	14160	0,81349	-16.68411	-16,49325	63.59	14.01	30,58	1.76270	0.33183
() - H (CH) (II)	. :	u i	3	۵	0	-152,34487	0.91771	0.86339	-15,75493	-15.56407	77.49	102.51	41.48	L3356.7	0 18709
(2) (5)		-0.9291M	-0.9291R	0	•	-153,47406	17719.0	0.81549	-16,63412	-16.49724	TA 22	1			
(i) (H) H = J.	ij	-0.9291X	-0.92918	-0.9291X		-154.40324	17716.0	0.77247	017.13.71-	1700			17.00	1.55486	0.29933
H,C,C,H,C,H,-	ن	-0 92918			,				11,0131	mp77s'/ -	91,10	06:811	3137	1.42988	0.37326
H.C.C.H.C.H. –	1				,	/1886.2cl-	17716.0	0 86359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	0.38106
(C(.(a))	ئ	-0.92918	40.9291R		•	-153,47406	17716.0	0.81349	-16 68412	-16,49325	56.41	12.59	× 684	00400	
$R = H_1(L_1, C_1)(H_2(L_1, -R_1)H(H_2, -R_2)$	ษ	316Zh O*	BIOCO D.	A GOOD OF										DEMOC.	0.45117
((-c. (b))	4				,	-136,411324	1719.0	0.77247	-17,61330	-17,42244	28,30	131.70	21.90	1.97162	0.51388
K = H; ('K = H; C,')C, (K = H; C,')CH; = (C, -C' (c))	ť	-0.92918	-0.72457	-0.72457	-0.72457	-134.71860	17716.0	0.75899	17.92866	-17.73779	48,21	131.79	21.74	71261	0.505.0
$ixiC_{\mu}C_{\mu}(H_{\mu}C_{\mu}-R)HCH_{\mu}-IC_{\mu}C_{\mu}C_{\mu}C_{\mu}C_{\mu}C_{\mu}C_{\mu}C_{\mu}$	ڻ	-0.9291x	-0.9291K	A19291R	0	154.40324	12210	1,677.0	1161770						Neach
tam("(N"-H,C,)C,(N"-H,C,)(H, -									200	******	48,30	131.70	8	1,97162	0.51388
(cc.(e))	2	-0.72457	-0.72457	-0,72457	-0.72457	15451399	17716.0	0,76765	.17.92866	917.57.71-	50.04	129.96	27,66	29462	0.44258
$(C-C, (H_2C, -R')HCH_2 - (C-C, (f))$	ن ء	-0,72457	-0.92918	-0.92918	è	-154.19863	0.91771	0.78155	-17,4m869	-17.21783	32.78	137.33	2		
1mx, (R'-H;C,)C, (R'-H;C,)CH;-	ئ	-0.72457	-0,72457	-0,72457	13.77.457	900		132.10						(may)	0.47279
							111160	U. /h/h3	17.92866	877.71.	30.04	129.96	8.2	1,94462	0,49298

Parameters	(1.6)	() H.)	0=0	H(0)3-3	77	60 00	(E) W = (C)						
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		1//1/0	0.65393	0.94.771	0.91771	0.91771	0.91771	17716.0	17716.0	0.91771	0.91771	17710	177160
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	- 1	-	-	_	-	-	-	-	3	3	3	G)	0.5
V, (eV)	-72.03287	-35.12015	-111.25473	-30,19634	-107 3272R	-70 41476	26 12016	, , ,	-	-	-	-	-
V, (eV)	26,02344	12.87680	23.87467	0.808	29 07739	25 10000	23,14013	-26.77214	-28.79214	-29.10112	-28.79214	-29.10112	-29.101.12
T (aV)	21.95990	10.48582	42 87081	7 17433	77 63014	23.70002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
V_ (eV)	-10.97995	.5 24701	0701710-	716076	26,33914	21.000/2	10.48582	6.77464	6.77464	6.90300	6.77464	6.90500	6.90500
E(10 un) (eV)	- 4 67480	14 63480		01/00/5-	10.20937	-10,33337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
ΔΕ, ,, (40.10) (eV)) C		-14.03489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15.35946	-15,35946
(() m) (oV)	20075	,	-2.07893	٥	0	0	0	0	•	•	0	۰	0
(12) (21 11) (21	14.03489	-14.63489	2.69893	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15 56407	Ab035 91-	1625046
(w, w) (cr.)	-49.66437	-31.63533	-63.27074	-31,63534	-67.69451	-49.66493	-31,63533	-31 63537	75357 15-	3135311	21,606.22	02000	08666.61-
If (atom - atom, myp? AD) (eV)	0	•	-2.69893	-1.85836	0	G	•	1 04834	/CCC0.10-	5000016	1:03337	-31.63535	-31.63535
E, (sa) (eV)	-49,66493	-31.63537	996969	-11 40171	0370373	1077707	,	1.0000	1.63639	-1.44915	-1.85836	-1.44915	-1.44915
ω (10'3 rad/s)	7705.85	37.1750	110703		00,000	47.00493	-31,63337	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
E. (aV)	P1 265 91	15 01200	10024	23.3291	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (eV)	507400	0 24066	22.10034	13,33303	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
(cV)	0.15542	0.24900	-0.40804	-0.23966	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	96802'0	-0.16515	-0.16416	-0.16416
	(Eq. (13.458))	(Eq. (13.458))	(12)	(26)	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
E. (0r)	-0.07727	-0.07200	-0.30266	-0.19066	-0.22757	-0.14502	-0.07200	-0.10359	2007576	70510	0.10360	77	[2]
E. (CV)	0.14803	0.14803	0.11441	0.14803	0.14803	0.14803	10891 0	0 14803	0.14803	277000	0.10339	-0.10200	-0.10260
Fylory (cV)	49.81948	-31,70737	-66.57498	-33.68439	-67.92207	-49 R0996	31 20213	23 60233	0.14603	0.14803	0.14803	0.14803	0.14803
Emay 6, to no! (aV)	-14,63489	-14.63489	-(4,63489	-14 63489	-14 63480	14 63.00	-31.70737	25/45/5-	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
E (c. 17 141) (cV)	-13,59844	-13.59844	0	0	-13 50844	13 50644	13.50044	-14.03489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Entrum (eV)	7,83968	3,47404	7,80660	4 4 1461	29 107 67	7 03017	13.39844	0	0	٥	٥	0	0
					242100	1,63010	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3,91734

	la		l					
	Relative Em		0.00056	0.00039	0.00000	0.0000	0.00034	10000
	Experimental	Total Boad Energy (eV)	15.655	28.198	52.491	52.604	77671	101 170
	Calculated	Encry (cV)	15.64628	10.787.11	52.50251	52.60340	N. 97561	101,13331
	(J-C		۰.	- c	. 0	00	. 0	0
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Γ			T-	2	a l	٦		I			Ţ		Γ-						
	è.	>	1163	(formaldchyd	(acetaldchyde)	(seetaldehvde)	107 (propane)	112 (propane) 113.8 (butae)	(isobutane)	(burbae)	(isobutane)	109.8 (ecctaldehyde)			110.8	Company	i i	(Isobutane)	(isobulane)
9	į	7	116.17	115.52		0.531	108.44	110,49		110,49		109.50	109.44	109.44	110,67	7, 011			111.27
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9	٠. E	2						69.51		1569			70.56	25.					
	₹ <mark>(</mark> §			0		-1,65376	٥					•			-1.85836	0	0		-1.85836
,	s.		1,20470	1.06267	4,11	0.83472	1,15796			- · ·,	1	1.15796			0.81549	1.04887	1,04817		78
	٢		6.75	67.0	-	-	0.73					27.0			-	57.0	0.75		2.
J	;		_	_	-	-	-					-			_	-	-	-	-
ú	7		-	6.75			-					-	1		-	67.0	6.75	1,0	3
٠,	V V V V V V V V V V V V V V V V V V V		-	17716.0	0.85395	(Fg. (15.114))	-					-			0.81549	17716.0	171160	12216.0	-
ึง	Alona 1		0.63008	0.86339	0.81549	42.08.4	U.SR339				1	v. 460359			0.81549	0.87495	0.87495	0.87495	
Atom 2	Designation	(Table 15.3.A)	I	-	•	2	=				3	=			ສ	-	-	-	
I. C. Calendar	Alem 2		x	-[4.82573 C.	-13,61806	1	=				-	+	1	-16.62412	υ,	-[4,82575 C,	-14.32375 C.	-[4,82575	3
Atom	Designation	(Table 15,3,A)	ž		n	7					-				ม	s	5	5	
E Cambridge	Alam		-16,39019	.15.75493	-16.68412	-13,75493					-15.75493			-16 68412	ن	-15.55033 C,	-15.55033 C.	.15.55033	;
2c.	Alman (Q,)		3.5637	4.2269	4.3826	3,4232			-		3,4252		T		4,7958	4,1633	4.1633	4.7958	
26	(0)		2.09132	2,11323	2.27954	2,11106			_		117702				2.91547	2.11323	3.09711	2.90327	+
Zc,	(°		2.00132	2.86175	2.86175	2,11106		-			2,09711				7.91347	2,91347	2,91547	2.9(1327	
Accounting 2C 2C 2C 1000 Statement Revision Graduate G C C C C			(C, H, (O) (i))	U=(H)=U	0.2,22	Medicion /HC H		כנ"נ"כ"		Д.У.Н Т	CHC H	7.7.7	H,2,32	4C,C,C,	C.	ZC,C,H In C,			0000

KETONES $(C_n H_{2n} O, n = 1, 2, 3, 4, 5...\infty)$

The alkyl ketones, $C_nH_{2n}O$, each have a C=O moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal 5 methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The C=O and C-C(O) groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between 15 the $C2sp^3$ HO and the O AO or between two $C2sp^3$ HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3)=-14.63489~eV$ (Eq. (15.25)) and the O AO has an energy of E(O)=-13.61806~eV. To meet the equipotential condition of the union of the C=O H_2 -20 type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO~to~O)=0.85395$. The unpaired electrons created by bond breakage of the double C=O bond requires that two times the O2p AO magnetic energy E_{mog} (Eq. (15.60)) be subtracted from the total energy to give $E_D(Group)$ (eV) for C=O.

As in the case with aldehydes, $E_T(atom-atom, msp^3.AO)$ of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-2.69893 \, eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of

the energy contributions corresponding to a double bond, $-1.13379 \, eV$ (Eq. (14.247)), and a triple bond, $-1.56513 \, eV$ (Eq. (14.342)). The triple bond contribution includes the $C2sp^3$ HO electron of the C-C(O) bond in addition to the pair involved directly in the double bond with O. Consequently, $E_T(atom-atom,msp^3.AO)$ of the C-C(O)-bond MO is $-1.44915 \, eV$, 5 corresponding to the energy contributions of the two $C2sp^3$ HOs to the single bond that are equivalent to those of methyl groups, $-0.72457 \, eV$ (Eq. (14.151)). Since there are two C-C(O) bonds in ketones versus one in aldehydes, $C_{1o}=C_1$ in Eq. (15.52) for each C-C(O) ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mog} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Table 15.55. The symbols	of full chomat groups of arky then
Functional Group	Group Symbol
C=O	C = O
C-C(O)	C-C(O)
CH₃ group	$C-H(CH_3)$
CH ₂ group	$C-H(CH_2)$
ĊH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	$C-C_{(f)}$

ز		C-H (CH3)	$C-H(CH_1)$	Group	C=C(a) Group	C + C (b)	Group Group	Group	Group	Clored Crosses
+-	Group Grov 1.64920 1.671	1.67 1.67	E 22	1.67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
04856 1.05553	1.04856 1.0555	1.0555	-	1.05661	1.45744	1.45744	1.45164	1,45744	1.45164	1.45164
10974 1.11713	1.110974	1,1171	-	1.11827	1.54280	1.54280	58965.1	1.54280	1.53635	1,53635
1.107 1.107 1.107 1.117 1.117 (C-H propane) 1.117 (C-H butane) (C-H butane)	San San	1,107 (C-H pro 1,117 (C-H bu	рапе)	1.122 (isobutane)	1.532 (propanc) 1.531 (butane)	1.532 (propune) 1.531 (butane)	1,532 (propunc) 1,531 (butane)	1.532 (propaue) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
27295 1.29569	1,27295	1.29569	\top	1.29924	1,54616	1.54616	1.52750	1.54616	1.52750	1,52750
631590 0.63159	0.63580 0.63159	063159	l	0.63095	0.68600	0.68600	0.68888	009890	0.68888	0,68888

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Table 15.95. The MO	١
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Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones.	trical bond	parameters of a	ikyl ketones. R	R, R', R" are H or alkyl groups. E, is $E_r(alom - alom, msp', AO)$	r alkyl groups.	E_r is $E_r(atom$	- alom, msp _ 1	(0)							
	Atom	6,	E	E,	£7	Final Total	,	,2	Eradma	$E(C2sp^3)$	io	9	6,	ď	d,
		(eV) Bond i	(eV) Bond 2	(eV) Bond 3	(6V) Bond 4	Energy C2sp ² (eV)	(°c)	(%)	(eV) Final	(eV) Final	€	© 	© 	(°)	(°)
R.C.H. (RC.H.)C. = 0	0	-1.3696	0	0	0		1.00000	0.84115	16.17521		136.09	43.91	55.72	0.53955	0.60595
R'C,H3(RC,H3)C, = 0	٠,	-1.34946	-0.72458	-0.72458	Б	-154.41430	17712.0	0,77199	-17,62437	-17.43350	133.02	46.98	61.86	0.61878	0.52672
H,C, -C, (O)(R')	ائن	-0.72458	0	0	o	-152,34026	17716.0	0.87495	-15,55033	-1535946	13.62	106.38	34.98	1.67762	519975'0
RH,C, -H,C, -C,(O)(R')	ئن	-0.72458	-0.92918	0	0	-153.26945	0.91771	0.82562	-16,47951	-16.28865	67.40	112.60	31.36	1,74821	0.31734
C - H (CH3)	Ü	-0.92918	0	0	o	-152,54487	17719.0	0.86359	-15.75493	-15.56407	77,49	102.51	41.48	1.23564	0.18708
C - H (CH ₂)	i	-0.92918	-0.92918	0	0	-153,47406	17716.0	0.81549	-15,68412	-16.49325	68.47	111.53	35.64	1.35486	0.29933
	i	-0.92918	-0.92915	81626.0-	0	-154,40324	17716.0	TASTT.0	-17,61330	.17.42144	61.10	118.90	11,37	1.42988	0.37326
H,C,C,H,CH, -	υ,	-0.92918	0	o	0	-152,54487	17716.0	0.86359	-15.75493	-15,56407	63.82	116.18	30.08	6,818,79	0,38106
$H_iG_iG_iH_iGH_i - G_iG_iG_i$::"	-0.92918	81626.0-	0	c	-153.47406	171160	0.81549	-15.68412	.16.49325	56.41	12.59	26.06	1,90800	0.45117
$R = H_2(\mathcal{G}_{\nu}(H_2C_{\nu} - R))HCH_2 - (C - C(b))$	ن ^ر	-0.92918	81626.0-	.0.9291 3	6	-154,40324	17718.0	0.77247	-17,61330	-17,42244	48.30	131.70	06.15	1,97162	0.51388
$n - H_1C_s(R' - H_2C_s)C_s(R'' - H_2C_s)C'H_1 - (C' - C'(c))$	ڻ	-0.9291R	-0.72457	-0.72457	-0.72457	-154.71860	17716.0	0.75889	-17.92866 .	-17.73779	48.21	131.79	21.74	1,95734	0.50570
$hoC_{\alpha}(A,A,A,A,B,B,B,B,B,B,B,B,B,B,B,B,B,B,B,B$	ť	-0.9291B	81626'0-	\$1626'0-	o	-154 40324	17716.0	0.77247	-17.61330	.17.42244	48.10	131.70	21.90	1,97162	0.51388
$IGH(C_{s}(R-H_{s}C_{s})C_{s}(R^{n}-H_{s}C_{s})CH_{s}-$ $IGH(C_{s}(R^{n}-H_{s}C_{s})CH_{s}-$		-0.72457	18427.0-	-0.77457	-0.72457	-154.51399	17116.0	6,76765	-17.92866	.17.73779	50.04	129.96	37.66	1.94462	0.49298
(נ, – נ; (U) ופענ'נ' (H'נ' – אֵי) אנאי –	C,	-2,72457	\$1626'D*	-0.92918	ა	-154,19863	17719.0	0.78155	-17,40869	.17.21783	52.78	77.721	24.04	1.92443	0.47279
$(R - H_2C_s)C_s(R^{-} - H_2C_s)CH_2 - C_2C_2(R^{-} - H_2C_s)CH_3$	ರ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76763	-17.92866	67.771-	\$0.04	129.96	32.66	1,94467	0,49298

Table 15,96. The energy parameters (eV) of functional groups of alkyl ketones.	rs (cV) of function	nal groups of alkyl	ketones.								,
Parameters	0 U	C-c(0)	£	C#,	#-0	(e) (c) (c)	(a)	C+C (c)	(g)	(e) (-)	(i) 2-2
	Croup	digo 5	Group	Group	dnoro	Group	dnoso	dion	Grap	diono	Group
n,	2	ı	3	2	-	1	1	-	1	1	-
n,	٥	0	2	-	0	0	0	0	0	0	0
n,	0	0	•	0	0	o	0	0	0	0	0
	0.5	0.5	0,75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
5		-	_	-	1	1	1	1	1	1	1
6.	-	-	-	-		-	1	1	1	1	1
ร์	0.85395	11116.0	12216'0	17716.0	17716.0	0.91771	177160	0.91771	177160	17716.0	0.91771
6,	2	0	0	-	ı	0	0	0	1	1	0
5	4	2	_	-	-	7	7	2	2	2	2
5	0	0	3	2	1	0	0	0	0	0	0
	0.5	1	27.0	0.75	54'0	5.0	. 20	5.0	5.0	5.0	5.0
ر:"	_	_	_	1	ı	1	1	1	1	1	1
V, (cV)	-109.17602	-30.19634	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (oV)	23,75521	9.50874	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9.33352	9,37273	6.37273
T (eV)	41.60126	7,37432	32.53914	21.06675	10.48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
V_ (eV)	-20.80063	-3.68716	-16.26957	-10.53337	-5.24291	-3.38732	-3,38732	-3.45250	-3.38732	-3.45250	-3.45250
E(no 10) (eV)	0	-14,63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15,35946	-15,35946
ΔΕ _{11,110} (.r. 10) (eV)	-1,34945	. 0	0	0	0	0	0	0	0	0	0
$E_T(\omega_{ii}\omega)$ (cV)	1.34946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
$E_r(u_s, \omega)$ (eV)	-63.27071	-31.63534	-67.69451	-49,66493	-31.63533	-31,63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
F_{τ} (01011 - 01011, 1150) (cV)	-2.69893	-1,44915	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1,44915	-1.44915
E. (120) (cV)	-65.96966	-33.08452	-67.69450	-49,66493	-31,63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
(s/pai 101) a	\$7.0928	16.4962	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
Ex (eV)	37,57947	10.85807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
En (eV)	-0.40003	-0.21568	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
F.cm. (aV)	0.21462	0.14655 [28]	0.35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312 [2]
E (vV)	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
(dV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(imp)$ (cV)	-66.55510	-33.22692	-67.92207	-49.80996	-31,70737	-33.59732	-33,49373	-33.24376	-33,59732	-33.18712	-33.18712
15 cm, (1, 40 no) (aV)	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489
Ermafr. w and (eV)	0	O	-13,59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{ij}(\omega_{ij})$ (aV)	7.78672	3.95714	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy E_{ac} that is subtracted from the weighted sum of the $E_{b}(b_{ca})$ (eV) values based on composition is given by (15.37).

Formula Section C.—C. (c) C.—C. (d) C.—C. (e) C.—C. (e) C.—C. (e) C.—C. (f) F.—C. Calculated Exercised Repetition Solution is given by (15.37).

1_	1 1			г		Γ-					_	_	Ι			
Relative Error	0.00031 0.00003 0.00003 0.00003 0.00003 0.00003 0.00003 0.00003 0.00003 0.00003		Exp. θ (°)	116.0 (acctone)	113.5 (2-butanagne)	121.9 (2-butananne)	107 (propens)	112 (propane) 113.8 (butene) 110.8 (sobutane)	(butane) 111.4 (sobutane)	108.5 (acelone)			(10.8 (Isobutane)		111.4 (isobutane)	111.4
Experimental Total Bond Formy (eV)	Emergy (eV) 12.14 13.14 14.997 15.18 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138 17.138		.j. (€)	115.77	113.71	122.07	108,44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27
	1		0° ©													
Calculated Total Bond Formy (nV)	40,6847, 25,84247, 65,60012, 65,00012, 65,00012, 65,00012, 65,10101, 77,15782, 77,15782, 77,2847, 77,2847, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31552, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522, 89,31522,		· (e)													
E			ø, ⊙			_		. 69.51	69.51		70.56	70.56		_		
<u>c-c (i) 7</u>	00000000000000000		E _r (eV)	-1.85836	-1.85836	-1.44915	0			0			-1,85836	0		-1.85836
1		(OF. dsm	٧ .	0.81549	0.81549	0.86445	1.15796			1.15796			0.81549	1.04887	1.04887	1.04117
(a) 2-2		is $E_{T}(arom-arom,mxp^{3}.AO)$	5	-	-	-	0.75			57.0		-	-	57.0	0.75	0.75
(p) 2-2	000000000000000000000000000000000000000	13	ů,	-	-	-	-			-			_	-	-	-
(c) C (c)	00000000000000000	ile were used.	' ⁵	-	-	_	-			ı			-	87.0	0.75	57.0
C-C (b)	000000000000000000000000000000000000000	preceding ang	C, Atem 2	0.81549	0.81549	0.\$5395 (Eq. (15.114))	-			-			0.81549	17719,0	17716.0	17716.0
C-C (a)	0-110000-044-0000	neters from the	Cy Abm I	0.81549	0.81549	0.87495	0.86359			0.86359			0.81549	0.87495	0.87495	0.87495
#5	000-00-00000000000000000000000000000000	Table 15.98. The bond sngle parameters of alkyl ketones and experimental values [1]. In the calculation of $ heta$,, the parameters from the preceding angle were used.	Atom 2 Hybridization Designation (Table 15.1A)	22	n	0	н			н			\$2	-	_	-
CH,	0 - n n o n n - o o o o n	the calculati	F. Cadeada Aom 4	-16.68412 C,	-16.68412 C,	-13.61806	Ξ			н			-16.68412 C,	-14.82575 C,	-14.82575 C _c	-14.82575 C
CH,	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	ntel valuos [1]. Ir	Atom I Hybridization Designation (Table 15.3.A)	22	25	3	7			7			25	~	٧,	۶
Group	000000000000000000000000000000000000000	and experime	Eradonia.	-16.68412 C.	-16.58412 C.,	-13.55033	-15.75493			-(5.75493			-16.68412 C.	-15.55033 C,	.15.55033 C,	-15.55033
C=0 Group		cyl ketanes r	2c' Teminal Alona (Q,)	4.8477	4.8374	4.5166	3,4252			3,4252			4.7958	4,1633	4.1633	4.7958
	9	neters of all	2c' Resd 3 (0 _e)	2.86175	\$1198.1	00162.5	2.11106			1,09711			2.91547	2.11323	2.09711	2,90327
Name	Acatone - Betwoore - Betwoore - Perturbore - Methyl-2-betwoore - Hetwoore - H	i angle para	2c' bend 1 (o',)	2,86175	2.91547	2.86175	2.11106			1.09711			291547	295167	2.91547	2,903.27
da.	1	15.98. The bond	Abons of Aspla	שניני"וסאני	(0)"2"2"	0,3,32	Methysan: ZHC.,H	לכ"כ"כ"	ZC,C,H	Mctait ZHC,H	ZC,C,C,	K,C,H	رد'ر'د' الله د'	ДС,С,Н № С,	LC,C,H == C,	רכיינ"ג" קביינ"ג"
Formula	000000000000000000000000000000000000000	Table		4	×											<u> </u>

CARBOXYLIC ACIDS $(C_n H_{2n} O_2, n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acids, $C_nH_{2n}O_2$, comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formic acid has a HC=O moiety that comprises a more stable C=O functional group and a CH functional group. All carboxylic acids further comprise a C-OH moiety that comprises C-O and OH functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that the energy of the C-H MO is matched to the carbon-atom contribution to $\Delta E_{H,MO}$ (AOIHO) and E_T (atom—atom, msp³.AO) of the C-O group. The alkyl carboxylic acid C=O and C-C(O) groups are equivalent to those given in the Aldehydes section except that \overline{E}_{Knh} is that of a carboxylic acid. The formic acid C=O group is solved equivalently to that of the alkyl carboxylic acid group, except that $\Delta E_{H,MO}$ (AOIHO) and E_T (atom—atom, msp³.AO) correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the C=O MO due to the presence of a H bound to the carbonyl carbon. Also, \overline{E}_{Knh} is that corresponding to formic acid. The C-O and OH groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the C-O MO is matched to that of the C=O group and \overline{E}_{Knh} is that of a carboxylic acid. $\Delta E_{H,MO}$ (AOIHO) of the C-O group is equal to E_T (atom—atom, msp³.AO) of the alkyl C=O group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones, $E_T(atom-atom, msp^3.AO)$ of the C=O-bond MO in Eq. (15.52) of alky carboxylic acids due to the charge donation from the C and O

atoms to the MO is $-2.69893 \ eV$ which is an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, $-1.13379 \ eV$ (Eq. (14.247)), and a triple bond, $-1.56513 \ eV$ (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl $C2sp^3$ HO electron with the O of the C-O-bond MO in addition to the pair involved directly in the double bond with the carbonyl O.

 $E_T(atom-atom,msp^3.AO)$ of the formic acid C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-3.58557\,eV$. This is also an energy minimum for the double bond between the pair of $C2sp^3$ HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a triple bond, $-1.56513\,eV$ (Eq. (14.342)), and a quadruple bond, $-2.02043\,eV$ (Eqs. (15.18-15.21) with s=4)) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a H bound to the carbonyl carbon.

 $E_T(atom-atom,msp^3.AO)$ of the carboxylic acid C-C(O) group is equivalent to that of alkanes and aldehydes, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the $C2sp^3$ HOs of the carboxylic acid. As in the case of aldehydes, $C_{1a}=2C_1$ in Eq. (15.52).

 $E_T(atom-atom,msp^3.AO)$ of the carboxylic acid C-O group is equivalent to that of alkyl alcohols, $-1.85836\,eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513). $E_T(atom-atom,msp^3.AO)$ of the C-O group matches that of the C-C(O) group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each E_D (Group) of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(G_{map})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	C – H (i)
C-C(O)	C-C(O)
C=O (formic acid)	C = O (i)
C=O (alkyl carboxylic acid)	C = O (ii)
(O)C-O	C-O
OH group	ОН
CH₃ group	$C-H\left(CH_{3}\right)$
CH ₂ group	$C-H$ (CH_2)
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

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ole 15.101. The MO to HO intercept geometrical bond	neidal bon		parameters of olkyl carboxylic acids. $R_i H_i R^n$ are H or olkyl groups. E_i is $E_i \left(a t a n - a t a m_i m \eta p^2 A O ight)$	acids. R.H.R"	are H or alkyl	groups. E, is	E, (atens – ata	м,ттр АО).						•		
2	Atom	ارج) (eV) Bond i	E _r (eV) Bond 2	E, (eV)	E, (eV) Bond 4	Final Total Energy ('2.pp'	[]	[3 (g)	Economic Final	E(C2.po') (eV) Final	g. (•)	, (C)	, (°)	d, (a,)	(o,)	
H-0(0)	9	41929JR	=	-	· c	હુ	1.00000	0.86359	.18.75493		115.00	16.19	6.13	0.55182	0.30025	
HO-(O)*	0	4162617	5	-	c		1 annan	0 186359	-15.75493		CC 101	20 11	48.58	1,14765	D 16993	
HU-(0)*	U	4192918	AT201.1.	c	c.	-154.3,7465	14716.0	0.77516	£17.42.71.	-17 356.85	73.74	90.9%	13.24	1.26386	0.053.29	
1,C.C. (0) - OH	0	41.92.918	6	5	c		1.0000	0.85359	.15.75493		101.32	73.63	48.58	1.14765	0.16950	
1,ς,ς, (υ)-он	j,	MIGEG TO	7.349.In	\$1626'O	c	-154.82352	17719.0	0.75447	-(R.0335#	-17 84271	91.96	AR CL	61,90	1,29138	0.02578	
$O = (HO)_{+}$	е	KT297.1-	o	0	c		0,0000	0.81871	.16.6183		137.10	42.50	65.45	0.53635	0.59978	
O = (HO) = O	ij	.1.7427X	A92914	c	. с	.15433766	17716.0	0.77536	47.54772	28925.11.	135.24	94.76	63.02	0.58361	0.53053	
$A_{i}^{*}H_{i}^{*}C_{i}^{*}(OH)=0$	٥	946401-	=	c	c		1,10000	0.84115	12241 29.		15.721	47.73	1699	0.52193	061784	
$H_1C_n(OH)=O$ = $O(Gh)$	Ü	11,34946	402918	40 9 2 U IX	c	SULFEST.	144160	0.754.7	-18 03358	17 84271	13.47	46.53	61,46	0.62072	0.51905	
-cropon H (In		¥T£97.1.	KI68617	6	В	.15433766	14116.0	37.576	.m2.tl.	58521.71-	69.80	110.11	36.00	1,30373	0.15661	
4.C C.(O)OH	٠٠	40,02918	3194£.1.	A1929.IX	c	-134 82352	0.01771	0.754.17	-18.03358	17518 71-	56.25	123.75	15.57	1,85002	0.41913	
C, - C, (0)0H	٠,٠	4,92918	c	5	o	15254487	141160	0.86359	15.75493	-15,55407	12.27	107.73	34.17	1.693#8	0.26301	
1,C,H,C, - C, (0)0H	2	*10TG'0-	#19 <u>7</u> 911.	5	0	153,47105	17716.0	กลเรษา	-16 (34)	-16,43325	63.99	10'71	30.58	0,76270	0.33783	
-H (r.H.)	Ŀ	*1656 tr			0	TALLE SLINT	0.91771	0,86359	-13,73493	15.56477	77,49	102.5[11.68	1,21564	0.18703	
-H (CH;)	į	*1020,D	#1676 UT	·	0	Sutre, ESI.	1221670	GESTEN	-16.58412	.16 49325	68.57	(1.13)	15.84	1,35486	Q.19913	
-H (CH) (B)	i	KINEU.	4162670	816I¢ U*	ė	-154,40324	122160	נאבנונט	-17 61330	-17.43344	61,10	118,90	31.37	1,429%8	0.37326	
C.C.H;CH;	ئن	-0 9291x	e	0	0	THEFTS!-	177100	u86359	-15.75493	-15.56407	63.83	116,18	30.08	1,85879	0.38176	
-(',C,H;C'H;	ن	#16 <u>2</u> 6.0-	41620.0-		e	50171.621.	12219:0	6ศ\$!มา	-16(84)2	£££6r 91-	17'95	(13.59	36.06	1,50800	0.45117	
$-H_1C_2C_6(H_4C_6-K)MCH_1-C_2C_2(h)$		#16tú'u-	#1629.ts	A.92918	c	-134,40324	171168	FL4TT.0	-17,61330	PFC2F'21-	0(3)	131.70	21.90	1.97162	0.51.388	
$-H_1C_2(R-H_2C_2)C_3(R-H_2C_2)CH_1-C_2(C_2)$	υ*	#16ZG:D*	78.457.04	40.72457	0.72457	-(34,718/G	17716.0	0,75889	-17,928%	-47.7379	48,31	131.70	21.74	1.95734	0.50570	
$C_{i}C_{i}(H_{j}C_{i}-R)HCH_{i}-C_{i}G_{i})$	ئن	#16ZG:0+	×16560-	40.9291R	o	-154,40024	17710-0	14577.0	ינגוטנוי	11,41344	48,30	131.70	21.90	1.97162	0.51368	
$K_{i}(R^{-}H_{i}C_{i})C_{i}(R^{-}H_{i}C_{i})C_{i}H_{i}-$	ئ	78127.02	13 LE 2 0°	-0.72487	.0.73457	-15451379	17719.0	0.76765	-17.93856	61727 51.	50.05	129.96	22 66	1.54462	0.19198	
n', c', (H, c', - R') HCH, -	ئ	ister	HICZL D-	A.929(X	ė	-151,19163	12216'0	0,78[55	(eHar't):	נמלוב, לן.	\$7.55	27.71	ភភ	1.92443	0.777.0	
$K'_{*}(W-H_{*}C_{*})C_{*}(W-H_{*}C_{*})CH_{*} - C_{*}CO)$	ď	RKIL	r\$ECT,0.	18551.0-	-0.72457	154.51399	17710-0	6.76763	-17.0284A	6ננמ נו−	75.55	139.96	33.06	1.94462	Q.47298	

Parameters ($C = C(0)$) $C = C(0)$ ($C = C(0)$) $C = C(0)$	() H)	(C)-C	C=0 (i)	.1	0-3	HO	CH.	CH.	(J-H (II)	(L-C (A)	(Q) J-2	(c) C-C	(P) .)-;	(3))-1	(C)
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ហី	17716.0	17716.0	0.85395	0.85395	0.85395	-	14416'0	14416'0	177100	122120	17716.0	12216.0	12216'0	17716.0	17716.0
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ť.)	0.75	-	0.3	0.5	0.5	0.75	67.0	54'0	0.75	0.5	5.0	5.0	5'0	5.0	5,0
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(.10) 1	-36,74167	-30,19634	-112,61934	-111.25473	-35.08488	-40.92709	107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	+1261.82-	-29.10112	-29.10112
V, (0F)	13.11890	9.50874	23.95107	23.87467	10.32968	14.81988	38.92728	20087.22	12.87680	9,33352	933352	67272.9	tseero	9,37273	637275
T (eP)	11.38634	7,17432	43.62389	42,82081	10,11150	16.18567	32.53914	21.06675	10.48582	6.77454	6.77464	6,90500	6.77464	6.90500	6.90500
1', (aV)	-5.69317	-3.68716	-21,81195	-21.41040	-5.05575	-8.09284	-16.26957	-10.53337	-5.24291	3.38732	-3.38732	-3.45250	-1,38732	-3,45250	-3.45250
Elmino (el')	-14.63489	.14.63489	0	0	-14.63489	-13,6181	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-1535946	-15.56407	-1535946	-15,35946
DEutoninom (ct)	-0.92918	0	-3.58557	-2.69893	-2.69893	0	0	0	0	0	0	0	0	0	0
K, (so no) (el')	-13.70571	-14,63489	3,58557	2,69893	-11.93596	13.6181	15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-1535946	-15.56407	-1535946	-15,35946
Er (4,20) (el')	-31,63530	-31.63534	-63.27075	-63.27074	-31,63541	-31,63247	-67,69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31,63535
E, (atom - atom, map', AO) (eV)	0	-1.85836	-3.58557	-2,69893	-1.85836	0	0	O		-1,85836	-1.85836	-1,44915	-1.85836	-1,44915	-1.44915
Ertical (eV)	-31,63537	-33.49373	-66.85630	-65.96966	-33.49373	-31,63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33,08452	-33.08452
(10, cad/s)	26.0575	1925.62	1856'09	59.4034	24,3637	44.1776	24,9286	1872,25	24.1759	9.43699	9.43699	15.4845	6698+16	9.55643	9.55643
E. (el')	17.15150	15.35563	40,12366	39,10034	16.03660	29,07844	16.40846	18,97831	15.917.99	6.21159	621159	10.19220	651179	6.29021	6.29021
En (41')	02652.0-	-0.25966	-0.41891	-0.40804	-0.26535	-0.33749	-0.25352	-0.25017	-0.24966	-0.16515	-0.1651.5	-0.20896	-0.16515	-0.16416	-0.16416
Ens (ct.)	0.3553 (Fo (13.458))	0.10502	0.21945	0,21077	0,14010	0.46311	0.35532	75555.0	0.35332 (Fn (13 458))	0.12312	0.17978	0,09944	0.12312	51251.0 151	0.12312
E_ (eV)	-0.08153	-0.20715	-0.30918	-0,30266	-0.19530	-0.10594	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	09701.0
E. (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803
E, Inmel (ell')	-31.71690	-33.70088	-67,47466	-66.57498	-33.68903	-31.74130	-67,92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Eury b, w in (ct)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-13.6181	-14.63489	-14,63489	-14.63489	-14.63489	-14.63480	-14,63489	-14.63489	-14.63429	-14.63489
County to as ind (cf.)	-13.59844	o	0	0	0	-13.50844	-13.59844	-13.59844	-13,59844	0	0	اه	0	0	0
$E_n^{(\mathrm{theory})}(cV)$	3.48357	4,43110	8.70628	7.80660	4,41925	4,41035	12,49186	7.83016	3.32601	4.32754	4.29921	3.97398	4,17951	3.62128	3.91734

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Εφ. <i>θ</i>	124.1 (formic ecist)		(firmle szé)	(formic acid)	136.6	110.6 Cicario con		(argrand)	(500 pt.) (500 pt.) (500 pt.) (500 pt.) (500 pt.)	(Setuna) (Setuna) (Setetime)	108.5 (acclone)			1101 (Bohutana)		111.4 (behama)	111.4 (sehutane)	
	13.68	110.76	123.44	107.71	125.70	109.63	126.03	108.44	110.69	110.49	05.001	109.44	109.44	110.67	110.76	111.20	111.27	05 20
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و رقع آخ		c	-1,44915	0	92591-	-1,44915	-1,44915	c			c			-1.85836	c	0	9(1837)-	
٧.	0.976.0	0 97(00	0,84115	1716.0	0.R3472	0.85877	0.0337	1.157%			1.137%			0.81540	1.04897	1.Darest	(DMR7	
ů,	6,75	67.0	-	2.75	-	-	-	6,73			6.75			-	87.0	67.0	27.0	
Ű	-	-	-	-	-	-	-	-			-			-	-	-	-	
Ü .	4.75	27.0	-	0.75	-	-	-	-			-			-	67.0	67.9	87.0	
C ₂ .	045395 (Eq.(15.114))	0.83195 (Eq. (15.114))	0.86359	Q91774	(Eq. (15.114))	043395 (Eq. (15.114))	981910	-			-			0,81549	0.91771	0.9171	17716.0	
1 mg	4,171495	0.87495	0.X1X71	-	041540	0.MU39	811740	n.wctsv			GENTO			0,81549	0.87.495	0.87495	\$0r1#0	
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Įį.	-13.61906	-13.618.06	-15.73495	-14,12575	-13,61806	13.61 100	(0,000)	×			Ξ.			-16,684f2 C.	, crayars	الايم <i>ي</i> ء ري	-14,82575	
Aken 1 Hybridization Pasignation (Hable 15.3.A)	•	۶	n	ı	7.		ū				7			ы	\$	s	\$	
f. man	-15.55:03	.15.55m3 C.	-16.61833 D,	-14,81573	116.08411	-15.75433	10, 1750 ()	-15,75493			15.75.93			-tadest2 C,	.15.55tt3 C,	.15 ssem	-15 55ms	
20 N= (0,)	3 7316	3100.1	17267	3.640\$	4,5026	1,1544	4 3818	3 4251			1422			4.795x	4.1633	4,1633	4,7958	
36' (a,)	12727	זמשנ	זעשעע	1,10616	127754	LATURE	16431	21105			117601			2.91547	20112	11460-7	19003	
2c' (a,)	3,005978	105398	1.77.17	1.6431	2,46175	2.95(1)5	2 27954	בווות			11/20/1			2,91547	191547	271547	1,90317	
-Vertical Angle	CH (i): C = 0 (i)	(CH (I))	70'C.0"	CH (0; C=0 (0))	d',C,O,	رد.'د 'ه'	40,CO.	H". HT	אנ'נ'נ'	H*5'.)7	ZHC, H	7.7.7.7	A'C'H	,5 -4 + C,	ZC,C,H	4.2.H	יים נ" קנויניני	7,5,5,7

CARBOXYLIC ACID ESTERS $(C_n H_{2n} O_2, n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acid esters, $C_n H_{2n} O_2$, comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formic acid ester has a HC = O moiety that comprises a more stable C = O functional group 5 and a CH functional group. All carboxylic acid esters further comprise a COR moiety that comprises a C-O functional group and three types of O-R functional groups, one for R comprising methyl, one for R comprising an alkyl ester group of a formate, and one for R comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups (CH₃) at each end of 10 the chain, and may comprise methylene (CH₂), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, 15 isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The CH functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester C = O and C - C(O) groups are equivalent to those given in the Carboxylic Acids section. 20 The formic acid ester C = O group is equivalent to that given in the Carboxylic Acids section except that \overline{E}_{Kvib} is that corresponding to a formic acid ester. The C - O group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state, \overline{E}_D (eV) and \overline{E}_{Kvib} , are those of a carboxylic acid ester. As in the case with the alkyl ethers, each O - C group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the O - C H₂-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the O - C-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO to O) = 0.85395$.

 $E_T \left(atom - atom, msp^3.AO \right)$ (Eq. (15.52)) of (1) the C = O group of alky carboxylic acid esters, (2) the C = O group of formic acid esters, (3) the alkyl carboxylic acid ester C - C(O) group, and (4) the carboxylic acid ester C - O group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are $-2.69893 \ eV$, $-3.58557 \ eV$, $-1.85836 \ eV$, and $-1.85836 \ eV$, respectively. $E_T \left(atom - atom, msp^3.AO \right)$ of the C - O group matches that of the C - C(O) group. Also, as in the case of aldehydes, $C_{1e} = 2C_1$ in Eq. (15.52) for the C - C(O) group.

 $E_T(atom-atom, msp^3.AO)$ of the O-C-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.13379\,eV$ for the $O-CH_3$ group of 10 formate and alkyl carboxylates, $-1.44915\,eV$ for the O-R group of alkyl carboxylates, and $-1.85836\,eV$ for the O-R group of alkyl formates, where R is an alkyl group. Each is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the $C2sp^3$ HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are $-1.13379\,eV$ (Eq. (14.247)), two times $-0.72457\,eV$ (Eq. (14.151)), and two times $-0.92918\,eV$ (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.108 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Table 13.103. The symbols of functional give	oups of alkyl carboxylic acid esters.
Functional Group	Group Symbol
CH (formic acid ester) group	C-H (i)
C-C(O)	C-C(O)
C=O (formic acid ester)	C = O (i)
C=O (alkyl carboxylic acid ester)	C = O (ii)
(O)C-O	C-O
O-CH ₃	O-C (i)
O-R (formic acid ester)	O-C (ii)
O-R (alkyl acid ester)	O-C (iii)
OH group	ОН
CH₃ group	$C-H$ $\left(CH_{3}\right)$
CH₂ group	$C-H\left(CH_{2}\right)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	<i>C – C</i> (e)
CC (t to iso-C)	C-C (f)

4	Lable 19.100. The Beamerinean Song parameters of any carooxylle acid esters and experimental values.	שמוויפורו או חושו	י במוסטעגוור פרוח ב	Sicra alla avperilli	Citat values 1.											
C-H (i) C-C(0)	-(0)	(C=0(i)	C=0 (ii)	C-0	0-0	O-C (ii)	0-c (iii)	$C-H(CH_s)$ $C-H(CH_s)$	C-# (CH;)	C-H (ii)	C-C (a)	(q) ン~ン	(e) C-C	(p) U-U	(e) U-U	(i) U-U
p.	Group	Oroup	Croup		Group	Group	Group	Oroup	Group	Oroup	Group	Group	Group	Group	Group	Group
1,61341	2.04740	1.290799	1.29907	1.73490	. 1.82683	1.78255	1,80717	1.64920	1.67122	1.67465	2.12499	2,12499	2.10725	2.12499	2,107.5	2.10725
1.03711	1,43087	1.13613	1.13977	1,31716	1.35160	1,33512	1.34431	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1,45164	1,45164
1.09763	1.51437	1.20243	1.20628	1.39402	1,43047	[,41303	1.42276	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
t. 101 (inethyl formate)	1,520 (scetic acid)	1.206 (methyl formate)	1,214 (acetic acid)	1,214 (ave. methyl formate)	(393 (avg. methyl formate)	1.393 (avg. methyl formate)	1.393 (avg. methyl fomnate)	1.08 (methyl formate) 1,107 (C - H propane) 1,117 (C - H butane)	1.107 (C – H propane) 1.117 (C – H butene)	1.122 (isobutane)	(buchne)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (gropane) 1.531 (butane)	1,532 (propase) 1,531 (butare)	1.532 (propane) 1.531 (butane)
123591	1,46439	0.61267	0.62331	1,12915	1.22901	1.18107	1,20776	1,27295	1.29569	1.29924	1,54616	1.54616	1,52750	1.54616	1.52750	1.52750
0.64281	0.69887	0.88018	187737	0.75921	0.73986	0.74900	0.74388	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

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DOOD	E	(eV) Bond I	ائر (د۷) Bond 2	رئم (وV) Band 3	(eV) Bond 4	Final Total Energy C2sp ⁴ (eV)	,} (e'	`3 <u>`\$</u>	(eV) Final	E(Czzp²) (eV) Final	% ©	e. ©	e. O	, (o,	ý° 😉	
RC,(0)0-C,H, (0-C f))	0	N102011.	.0.36690	G	С		1,00000	0,83360	-16.321k3		90.63	89.37	42.70	1,34246	0.00914	·
RC.(0)0-C.H. (0-C (i))	ď	06995,0-	ū	D	c	-152.18239	17716.0	0,8H392	-15.39265	-15.2017R	10.20	84.99	45.76	1,27445	0.07716	
HC,(O)O – C,H,C,H,R (O – C (ii))	o	-0.9291R	-0.9291K	o	С		1,00000	0.81349	-16,68412		93.09	16.91	43.59	1.29113	0.04399	<u> 4</u>
HC,(O)O-C,H,C,H,R (O-C (ii))	ئن	-0.9201X	*1020.0-	0	e	-153.47405	17616.0	0 K1549	-16,68411	-14,49325	93.09	16'98	43.59	1,29113	0.04399	
R'C, (0)0 – C,H,C,H,R (0 – C, (ii))	0	*1626.0-	-0,72457	c	e		1.0000	0.172562	16.47051		21.12	88.2K	43.10	131931	0.02480	
R'C,(0)0~C,H,C,H,R (0~C (ii))	ΰ	-0.72457	-0.9391k	0	c	-153.26945	17710.0	0.82562	-16.47951	-16,28864	21.12	88.28	43.10	เรแณ	0.02480	,
$HC_{a}(O) - OC_{b}H_{s}$ $(C = O \ (i))$ $(O - C \ (i))$	0	-0.92918	-0 36690	c	0		1.0480.0	0,833/0	-16.32183		72.82	81.03	46.82	1.18716	0.13000	
HC,(O)-OC,H, (C=0 (i)) (O-C (i))	C.	H1(26,0.	-1.79278	0	C	-154.33765	0.91778	0.77536	.17,54772	-17.35685	93.94	86,06	43.24	1,2/38%	0.05329	,
HC_(O) - OR (C = O (i)) (O-C (ii))	0	-0.92918	-0.925 (#	0	ū		1.00000	0.81549	-16,68412		97.48	12.57	£.73	1,11100	0.10616	
HC_(O) - OR (C = O (i)) (O - C (ii))	ن	FC297,1-	\$1676'U	c	c	יונאן.	17716.0	0.77536	2774271-	-17.35685	93.94	90'91	43.24	130%	0.05329	
R'H,C,C,(O)-OC,H, (C=O (ii)) (O-C (i)).	0	нго26:0-	06995'0-	c	G		1.00000	0.83360	.16.32183		98.57	81.03	46.82	1,18716	0.13000	
R'H,C,C,(0)-OC,H, (C=0 (ii)) (O-C (i))	С.	ж1626.0-	97676'1-	#1GZG.0-	c	-134,82352	17716.0	0.73447	-18,03358	-17.84271	96.196	88.04	D6:14	1,20138	0.02578	,
$R'H_2C_sC_s(O) - OC_sH_2C_sH_1R$ ($C = O$ (ii)) ($O - C$ (iii))	0	-0.929 FR	L5+7LT+		o		1.00000	0.82362	-16,47951		98.32	\$1.03	KB	1.19766	0.11949	
R'H_C,(0) - OC,H,C,H,R (C = 0 (ii)) (O-C (ii))	ڻ	81626.0-	-1.34946	-0.9291K	c	-154,82352	0,91771	0.75447	-18.03358	-17,84271	91.96	18.04	41.90	1,29138	0.02578	
HC_(OR) = O (C = O (i))	0	-1.79278	0	0	0		1,00000	0.61871	-16,61853		137.10	42.90	65.45	0,53635	0.59978	
HC,(OR) ≈ O (C ≈ O (i))	٠,	¥7207.1.	-Q92918	u .	0	-154.33766	0.91771	0.77536	-17.54772	-17.33685	135.24	44,76	63.02	0.58361	0.53033	
$R'C_*H_!C_*(OR) = O$ $(C - O(ii))$	0	9161E'1-	0	. 0	0		1.00000	0.54115	-16,17521		12.72	42.73	1599	0.52193	0.61784	
$R'C_{\mu}H_{1}C_{\mu}(OR) = O$ $(C = O(ii))$	ڻ	3404E -	-4.9291R	B1626'0-	ű	-154.82352	0.91771	0.75447	-18,03358	-17.84272	133.47	46.53	61.46	0,62072	0.51905	
н -с.(О):ОК (С.Н. б))	ı	1.7927.1	-0.92018	u	0	-15433766	0.91771	0.77536	-17.54772	-17,35685	69.89	11'011	36.09	1,30373	0.36662	
R'H,C, -C,(O)OR	٠٠	#16E6'0-	-1.341946	-0.92918	٥	-154,82352	0,91771	0,75447	-18.03358	-17,84272	56.25	121.75	75.82	1.85002	0.41915	
H,C, -C, (0)0R	ر ر	0.92918	0	0	•	-152.54487	0.91711	0,86359	-15,75493	-13.36407	72.27	107.73	71.7	1.69388	0.26301	
C-H (CH.)	;	-1,92918 -0,93918	*1626.0-		•	-153.474(15	0.01771	0.1(549	-16.68411	-16.49325	68.99	114.01	30.58	1.76270	0,331\$3	
C-H (CH;)		.D.9291R	-0.9291R	, a		-153,47406	0.91771	0,81549	-15,73493	-15.50407	17.49 84.47	102.51	35.84	13564	0.18708	
						1	1	1						1		

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid exters. R.R.R. R. are H or alkyl groups. Et is E.(ainm - arom, nxp², AO).

Bond	APAIN	,													
		(eV) Bond :	(eV) Bond 2	(eV) Bond 3	(eV)	Final Total Energy (2sp)	<u>[a</u>]] <u>e</u>	(eV)	$E(C2sp^3)$ (eV)	(•)	ø* ①	, (e)	g 'g	(a,)
						(eV)			!	E C		:	:	:	:
(= H (CH) (II)	۲.	-0.92918	-0.0291R	-0.92918	۰	-154,40324	17710.0	0,77247	-17.61330	-17,42244	61.10	00 311	27.17	BAULY	200
H,C,C,H,CH2 (C,-C, (a))	ن ن	-0.92918	0	0	٥	-152.54487	0.91771	0.86359	-15.75493	-15.56407	63.12	116.18	30.08	183879	0.31326
$H_1C_1C_2H_2CH_2 - (C_1-C_1(a))$	ť	-0.92918	R1626'0-	. 6	0	-153.47406	17710.0	0.81549	-16.68412	-16,49325	56.41	13.59	26.06	0,90190	045117
$R - H_2 C_s \left(H_2 C_s - R' \right) H C H_2 - \left(C - C_2 \left(b \right) \right)$	ن	-0.9291E	A.92918	#16Z6'0-	0	154,40324	0.91771	G,77247	-17.61330	-17,42244	48,30	131.70	21.90	1,97162	0.51388
H-H-JC, (H-H-JC), (H-H-JC), (H-H-JC)	ن	-0.9291E	-0.72457	-0.72457	-0.72457	.154,71860	17190	0,75889	-17,92866	617.57.71.	48.21	131.79	21.74	7,000	0.60630
10 L. C. (H.C 11) HCH															
((p) .)))	ت	.0.0201x	-0.92918	-0.92918	c	154,40324	0.91771	0,77247	-17,61330	-17,42344	48.30	131.70	21.90	1.97162	0.51383
(C'-C'(e))	۲,	-0.72457	-0.72457	-0.72457	-0,72457	.134,51399	0.91771	6,76765	-17.92866	947.71-	30.04	129.96	22,66	1.94462	0.49298
$her(C_{s}C_{s}(H_{s}C_{s}-R)HCH_{s}-C_{s}(C_{s}-C_{s}(0))$	ζ,	-0.72457	31626'U-	-0.9291x	đ	-134,17863	17716.0	0.78155	-17,40869	-17.21713	52.78	127.22	70'92	1.572443	0.47279
$(C'-C', (R'-H_3C_3)C_4(R'-H_3C_3)CH_3 - (C'-C', (0))$	ני	-0.724S7	-0,72457	-0.72457	-0.72457	-154.51399	17710.0	0.76765	-17.92866	.17,73779	\$0.04	120.96	22.06	1.94462	0.49298
												,			_

_	_				_		_	_	_	_											_		2)										
() 2-C		-	٥	٥	0.5	-	-	17716.0	٥	2		20	-	-29.10112	57775	00500 9	-3.45750	16.35046	0466661	16 36046	31 63636	-1,44915	-33 08457	9.55643	6.29021	-0.16416	0.12312	7700	-0.10200	0.14803	-33.18712	-14.63489	3 01734	,,,,,,
C-C (e)	-	- .	0	٥	0.5	-	ı	17716.0	-	7	0	20	-	-29.10112	0 37773	00500	.3.48750	35046	0	-16 35046	31,6363	-1.44915	-33.08452	9.55643	629021	-0.16416	0.12312	9	-0.10200	0.14803	23.18712	-14.53489	367128	
C-C (d) Group		- •	5	0	0.5	1	1	0.91771	-	7	0	20	-	-28.79214	9 33352	6.77464	-3.38732	-15 56407		-15 56407	21 63577	-1.85836	-33,49373	9.43699	621159	-0.16515	0.12312	0 10350	1,000	0.1400.3	75/60:00	-14.03469	4.17951	
C-C (c)	-	-	,	3	20	-	-	0.91771		2	٥	50	-	-29.10112	9,37273	6.90500	-3.45250	-15 35946	•	-15 35046	-3163535	-1.44915	-33.08452	15.4846	10.19220	-0.20896	0.09944	70 1 5074	0 1400	25.75	0/ 547 55	0 00403	3,97398	
C-C(b) Group	-			•	000	-	_	17716.0	0	2	٥	S	-	-28.79214	9.33332	6.77464	-3.38732	-15.56407	٥	-15.56407	-31.63537	-1.85836	-33.49373	9,43699	621159	-0.16515	0.17978	-0.07576	0 14805	23 40373	14 67490	0	4.29921	1
C-C (a) Group	-		, ,	> ;	20	-	-	0,91771	0	2	0	0.5	-	-28.79214	9.33352	6.77464	-3.38732	-15.56407	0	-15.56407	-31.63537	-1.85836	-33.49373	9.43699	6.21159	-0,16515	0.12312	0.10359	0 14803	.11 50717	╁	╁	432754	
C-H (ii) Group	-		•	, ,	0.73	-	-	17716.0	-	_	-	0.75	-	-35,12015	12.87680	10.48582	-5.24291	-14.63489		-14.63489	-31,63533	-	-31.63537	24.1759	15.91299	-0.24966	0.35532 (Eq.	-0.07200	0.14803	+	╁	┨	3.32601	
CH,	~	-		, ,	27.7	-	-	0.91773	-	-	2	0,75	-	-70.41425	25.78002	21.06675	-10,53337	-15.56407		-15.36407	-49,66493	۰	-49.66493	24.2751	15,97831	-0.25017	0.35532 (Eq.	-0.14502	0.14803	49.80996	-14 63489	╫	7.83016	
CH, Group	"	7	c	22.0	2.3	-	-	0.91771	•	-		0.75	-	-107.32728	38.92728	32,53914	-16,26957	-15.56407	0	-15,56407	-67.69451	0	-67.69450	24.9286	16.40846	-0.25352	0.35532 (Eq.	-0.22757	0.14803	-67.92207	-14,63489	-13.59844	12,49186	
O-C (iii) Group	-			٥	<u> </u>	-	-	0.85395	0	2	c	0.5	-	-33.15757	10,12103	9.17389	-4.58695	-14.63489	-1.44915	-13,18574	-31.63533	-1.44915	-53.08452	12,0329	7.92028	-0.18420	0.16118	-0.10361	0.14803	-33.18813	+	┢	3.91835	
O-C (ii) Group		٥	۰	9.0	-	_ .	-	0.85395	•	7	•	2,0	-	-33.78830	10.19070	9.47754	-4.73877	-14.63489	-1.85836	.12,77653	-31,63536	-1.85836	-33.49373	22,7749	14.99085	-0.25655	0.11469	-0.19921	0.14803	-33.69294	-14.63489	0	4,42316	
O-C() Group	-	٥	٥	0.5	-	-	-	0.85395	•	2	•	6.5	-	-32.67173	10.06642	8,94219	-4.47110	-14.63489	-1.13379	-13,50110	-31.63531	-1.15379	-32.76916	21.4553	14,12224	-0.24362	0.11469 [32]	-0.18628	0.14803	-32.95544	-14,63489	0	3.68.566	
C-O Group	-	٥	٥	0.5	-	-	-	0.85395		-	0	20	-	-35.08488	10,32968	10.11150	-5.05575	-14.63489	-2.69893	-11.935%	-31.63541	-1.85836	-33.49373	12,7926	8.42030	-0.19228	(32)	-0.11745	0.14803	-33.61118	-14.63489	o	4.34141	
C=O (ii) Group	2	0	o	0.5	-	- -	- 00	0.83395		•	0	50	-	-111,25473	23.87467	42,82081	-21.41040	٥	-2.69893	2.69893	-63.27074	-2.69893	-65.96966	59,4034	39,10034	-0.40304	0.21077 [12]	-0.30266	0.11441	-66.57498	-14,63489	0	7.80660	
C=0 (1) Group	2	0	0	2.0	-	-	- 0000	0.853995	,		3	3	-	-112,61934	23.95107	43.62389	-21.81195	0	-5.38557	3.58557	-63.27075	-3.58557	-66.85630	60.9581	40.12300	-0.41891	0.21747 [32]	-0.31017	0.11441	-67.47664	-14.63489		8.70826	
C-C(O)	-	0	0	2,0	-	-	122100	1//16	,	1	-	- -	+	#	9.50874	7,37432	-3.08716	-14.6.3489	•	-14.63489	-31.63534	-1.83836	-33.49373	23.3291	20000	-0.63,00	0.10502 [29]	-0.20715	0.14803	-33,70088	-14,63489	0	4.43110	
C-H (i) Group	-	0	0	0.75	-	-	122100		, -	-	- 6	2 -	-	-30./410/	13.11890	11.38634	/18/0.0.	-14.0.1489	-0.92918	-13.70571	-31,63530	0	1,65557	26.0575	00000	0.35532	(Eq. (13.458))	-0.08153	0.14803	-1	⊣	-13.59844	3.48357	
Parancters	r.	n_2	п,	ט	ن	ů.							1 (S)	7.50	1.6.10	(43)	(40)	() () () () () () () ()	(45) (m) (m) (m)	Er (40 10) (CV)	(ap) (ari)	E. (alom - atom, msp. AC) (cV)	(100 (cm) (cm)	# (av)	E (aV)	(eV)		E. (eV)				(4)	Cn(thum! (CV)	

Table 15.108. The energy parameters (eV) of functional groups of alkyl carboxylic acid esters.

we using the functional group composition and the energies of Table 15,108 compared to the experimental values (3). The magnetic energy E_{soc} that is subtracted from the weighed sum of the $E(L_s)$ to the	j l	
ompared to the	CH (II)	00000
Table 15,108 c	CH,	O D M 4 19 40
the energies of	CH,	- ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~
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en by (15.57).	C=O C=O (i) (ii) Group Group	
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values based on composition is given by (15	None Formate	Methyl peristo Methyl peristolic Methyl lexenosic Methyl lexenosic Methyl lectimosic Methyl octimosic Methyl octimosic
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	Relative																										0.0003	-0.00073	50000	0.00052
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מו ס'יי וווכ מאד	ű"]			0.KG599	0,81871	0,83360	0.84359							0.86359			0.81549	0.87495	0.87495		0.87495	
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() contra	A Company			-13.61106	-14.68412 O.	-18.47690 C.	Ξ						ľ	=			-16.6W412 C,	-14.82575 C,	-14.82575	ر.	-14.82575	
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	L'interior			-15.75493	-16.61KS3	-16.32183 C.	-15.75493							-15.75493			-16,68412 C,	-15.55033 C,	-15,55033	;	-15.35033 C.	
	Zc. Termbal	Almos (Gg)		3,9463	4,4043	4.4833	3433							3,4252			4,7958	4.1633	4.1633		4.795R	
	Zc.	<u>e</u>		1.70521	16460.5	1.63431	2,11106							7.097			2.91547	2(1323	2,097(1		2.90327	
	Bond	(°)		2.09711	1,27727	2.70321	2.11106						1.200	7.097			2.91347	2.91547	291547		2.90327	
Administration of the parameters from the preceding angle were used. 6; is E, (alon = alon are) AO			0 0117	$(CH_{1}(0); C=0 (0))$	(CH (0): C=0 (0)	CH (0): C = 0 (0)	Meanintone ZHC, H		, C, C, C,			н"5"57	Metho	ZHC, H	45,C,C,	H",","77	". ".". "".	J. O. J. D. J. D. J. D. J. D. J. D. J. D. J. J. D. J. J. J. J. J. J. J. J. J. J. J. J. J.	н, 22, 22, н	1	خدور ارد معد ر	, C.C.C.

AMIDES $(C_n H_{2n+1} NO, n = 1, 2, 3, 4, 5...\infty)$

The alkyl amides, $C_n H_{2n+1} NO$, comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formamide has a HC = O moiety that comprises a more stable C = O functional group and a CH functional 5 group that is equivalent to that of the CH (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso-CH group of branched-chain-alkyl portion of the alkyl amide except that E_{mog} (Eq. (15.58)) is not subtracted from $E_D(G_{mnp})$. All amides further comprise a $C-NH_2$ moiety that comprises a NH_2 functional group and two types of C-Nfunctional groups, one for formamide and the other for alkyl amides ($RC(O)NH_2$ where R is 10 alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH)functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain 15 alkanes. In addition, the C-C bonds within isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The NH₂ functional group was solved in the Dihydrogen Nitride (NH₂) section except 20 that the energy of the N-H MO is matched to the nitrogen-atom contribution to ΔE_{H₂MO} (AOIHO) and E_T (atom-atom, msp³.AO) of the C-N group. Both alkyl amide C = O groups and the C-C(O) group are equivalent to those given in the Carboxylic Acid Esters section except that \bar{E}_{Kvih} of the C-C(O) group is matched to that of an amide. The C-N groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the C-N MO is matched to that of the C = O group and \bar{E}_{Kvih} is that of a amide. $\Delta E_{H_1,MO}$ (AOIHO) of the C-N group is equal to E_T (atom-atom, msp³.AO) of the alkyl C = O and C-N groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each C - N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of

electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the C-N H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the C-N-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ N) = 0.91140$.

 $E_T(atom-atom, msp^3.AO)$ (Eq. (15.52)) of the C=O group of alky amides and the C=O group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are -2.69893~eV and -3.58557~eV, respectively.

 $E_T(atom-atom,msp^3.AO)$ of the amide C-C(O) group is the same as alkanes, 10 aldehydes, carboxylic acids, and carboxylic acid esters, $-1.85836 \, eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule, $E_T(atom-atom,msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation 15 from the C and N atoms to the MO is $-1.65376 \, eV$. It is based on the energy match between the $C2sp^3$ HO of the carbonyl and the primary amino group NH_2 . It is given by the linear combination of $-0.92918 \, eV$ (Eq. (14.513)) which matches the contiguous C-C(O) or HC(O) group and $-0.72457 \, eV$ (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.114 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	C - H (i)
C-C(O)	C-C(O)
C=O (formamide)	C = O (i)
C=O (alkyl amide)	C = O (ii)
(O)C-N (formamide)	C-N (i)
(O)C-N (alkyl amide)	C-N (ii)
NH ₂ group	NH_2
CH ₃ group	$C-H$ $\left(CH_{3}\right)$
CH ₂ group	$C-H$ $\left(CH_{2}\right)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

	7	7	1			Т	7
C-C (f)	100	27/01/2	1,53635		1,532 (propane) 1,531 (butane)		1.52750
(e) C-C	3 10735	1.46163	1.53635		L.532 (propane) 1.531 (butane)		1.52750
C-C (d)	2 17400	1 46341	1.54280		1.532 (propane) 1.531 (butane)	2020	01000
C-C (c)	2 10775	1 45164	1.53635		1.552 (propane) 1.531 (butane)	03/63	0.526.30
C-C (b)	2.12499	1 45744	1.54280		1.532 (properc) 1.531 (butane)	1 44616	O CARADO
C-C (a)	2.12499	1.45744	1.54280		1.532 (propane) 1.531 (butane)	1 84616	0.08600
C-H (ii)	1.67465	1.05661	1.11827		1.122 (isobutane)	1 29974	26000
C-H (CH1)	1.67122	1.05553	1.11713		(C-H propane) 1.117 (C-H	1.29569	0.63159
$C-H(CH_3)$	1.64920	1.04856	1.10974		1.107 (C - H propane) 1.117 (C - H	1.27295	0.63580
NH, Group	1.32297	0.97065	1.02729		1.027 (formanide) 1.022 (acetamide)	0.89894	0.73369
Group Group	1.75370	1,32427	1,40155		1.380 (acetamide)	1.14968	0.75513
C - N (i) Group	1.70920	1,30736	1.38365		1.368 (formamide)	1.10098	0.76490
O(i) $C=O(ii)$ $C-N(i)$ Oup Group Group	1,29907	1.13977	1,20628		(acetamide) 1.225 1.225 (N- methylacetamide)	0.62331	0.87737
<u>"</u> 5	1.290799	1.13613	1,20243		1.212 formamide)	0.61267	0.88018
C-C(O) Group	2.04740	1,43087	1.51437	9.5	(acctamide) 1.520 (N. methylacctamide)	1.46439	0.69887
Parameter C-H (i) Group	1.67465	1.05561	1,11827		1.125 (formanide)	1,29924	0.63095
Parameter	("0) 0	c' (a,)	Bond Length 2c' (A)		Exp. Bond Length (A)	1,c (a,)	

- Total								,							
ninc	E ST	(eV)	(eV)	(eV)	(eV)	Final Total Energy] <u>e</u>	´ſ <u>.</u>	Eradone (eV) Einel	E(C247) (eV)	. ₀ (C)	ø <u>.</u> ©	°, ©	, G	d,
n vinivolua						ું કુ				Final		;	•	:	•
$(C = O(i) \operatorname{and}(ii))$	×	-0 83688	9		•		0.93084	0.86923	-15.65263		1130	66.10	62.13	0.61843	0.35222
$HC(O) - \lambda H_3$ $(C = O \ (i))$ $(C - N \ (i))$	N	-0. K2688	e		۰		0.93084	0.16923	-15.65263		103.03	76.07	50.02	1,09214	0.20922
$HC(O) - NH_{z}$ (C = O (i)) (C - N (i))	·	-0 17611	-1,7927R	c	G	. (\$4.23535	17716.0	0.77991	-17,44541	-17,25455	3,4	13.19	44.70	1.21492	0.09244
$RH_3G_a(O) - NH_3$ ($C = O$ (ii)) ($C - N$ (ii))	N	-0,42688	p	6	c		0,93084	0.86923	-15.63263		100.14	79.16	4R.10	1.17127	α 15300
$RH_2C_a(O) - NH_1$ ($C = O$ (ii)) ($C - N$ (ii))	U.	-0.826ж	-1.34946	816260-	0	154.72121	0.91771	0.75878	-17.93127	-17.74041	90,51	89.49	4130	131735	0.00672
$HC_{a}(NH_{a}) = 0$ $(C = 0 \ ())$	0	1,79278	O	0	0		1.00000	0.81871	-16.61833		137.10	42.90	65,43	0.53635	0.5997#
(C=0 (i))	; ·	.1.7927ж	0,82688	a	0	-154,23535	0.91771	0.77991	-17,44541	-17.25455	135.44	44.56	63.28	0.58044	0.55569
$KC_{\mu}H_{1}C_{\mu}(NH_{3})=0$ (C=0)	6	1.34946	0	e e	0		1.00000	0.84115	-16.17521		137.27	42.73	66.31	0.52193	0.61734
(C=0 (ii))	ان	1,34946	-0.12688	-0.9291R	0	12127.481-	0.91771	0.75878	17.53127	11,34041	133.67	EE 99	61,70	0.61382	0.52395
н -с(О)ин; (Сн ())	ن	ж С 207.1-	-0.13611	0		-154,23535	0.91771	0.77991	11,44541	-17.25455	62.39	19711	32.13	1.41810	0.36148
ян,с, –с, (O) мн,	U,	-0.92918	1.34946	-0.826RR	0	-154.72121	0.91771	0.75878	17,93127	-17,74D41	\$7.02	12.51	25.76	1.843.66	0.41700
#,c, - C, (O) NH;	ان	-0.92918	۰	-	۰	-152 54487	0,91771	0.86359	-15.75493	15,56407	n.n	107.73	Z.A	1.69318	0.26301
C-H (CH)	ر ا	#1620.0-	-0.9291X	e	•	-153.474mS	17719.0	0.81349	16.68411	-16,49325	65,590	114,01	30.58	1,76270	0.33183
(C-H (CH)		810Z019	0	0	٥	-152.54487	0.91771	0,86359	-15,75493	15.56407	77.49	102.51	41.48	123564	0.18708
C = H(CH) (ii)	٠	A1020.0.	-0.92918	•	٥	-153,47406	17116.0	0.81549	-16.68412	-16.49325	68.47	111,53	35.84	133486	0.29933
- H3H33H	٥	KIRKIO-	-0.92918	-0.92918		154,40324	0.91771	0.77247	.(7,61330	17,42244	61.10	118,90	TEIE	1.42913	0.37326
((, ~ (, 0))	່ ບໍ	-0.9291R	B	c	c	-152.54487	17716.0	0.86359	-15,73493	-15.56407	63.82	116.18	30,03	1,83879	0,31106
(C'−C'(a))	ن	R10 <u>2</u> 0.0-	4,92911	0	, ,	-133,47406	17710.0	0.81549	-16.68412	-16.49325	36.41	123.59	26.06	OCROC!	0,45117
R-H3C,C,(H2C,-R')HCH2- (C-C (b))	ú	810Z6'0-	-0.92918	-0.92918	0	-154,40324	17716.0	0.77247	0.17,61330	-17,42244	48.30	131.70	21.30	1,971@	0.51388
R = H.ś.", (R = H.ṣ.),C., (R" = H.ṣ.,)CH.; = (C' = C. (c))	ئ	K1026'0"	-0.72457	-0.72457	-0.72457	-134.71860	17716.0	0.75889	.17.92866	07767.71-	12.	131.79	21.74	ME720.1	0.50570
(C'-C'(d))	ئ	N1020.0-	-0.92918	-0.92918	Đ	-154,40324	171160	0,77247	.17.61330	-17.42244	ος. ‡30	131.70	21.90	1.97162	0.51388
(C-C, (e))	່ວ່	-0.72457	-0 72457	-0.72457	-0.72457	66818'781-	17716.0	0.76765	.17.92866	errer.11.	\$0,04	120.96	22.66	1.944@	0.49293
(C-C,G)	ď	-0.724S7	-0.92918	-0.9291я	·o	-154,19863	0.91771	0.78155	-17.40869	-17.21783	52.78	17.73	24.04	1.92443	0.47279
$(C-C, \{B\})$	C,	-0.72457	-0.72457	-0.72457 -	-0.77457	-154,51399	17719.0	0.7676.5	-17.92866	.17.73779	50.04	96'62)	22.66	1.94462	0.49298
									1				_	_	

Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides. R.R.R" are H or alkyl groups. E, is E, (omm-utom, nsp',AO).

Parameters	0 17.7	9			13 11 2											
	C dnoud	Group	Care Care	C (B)	() A ()	C-7 (ii)	₩.	₹		(II)	(a) C-C	(4) D-2	(c) U-C	(Q) C-C	(e) U-U	0-0
11	-	-	,	.			Glaup	Quan	Group	dnois	drono	Group	Group	Сточр	Group	Group
	-	-	,	7	-	-	2	n	2	-	-	-	-	-	-	-
n3	٥	0	0	0	0	0	0	2	-	c	6		. ,			
4	0	0	٥	•	0	٥	-			,	,		5	-	В	٥
:	0.75	9.5	0.5	0.5	50	50	0.74	, 5		,		>	٥	٥	٥	0
::	-	-	-	-	-	}	7.00	2,7	0,,0	0.0	0.5	0.5	0.5	0.5	0.5	0.5
	-	. -	- -		-	-	0.93613	-	-	-	-	_	-	_	-	-
-	1	-	-	-	-	-	0.75	-	-	1.	1	1	_	-	-	-
	0.91//1	0.91771	0.85395	0.85395	0.91140	0.91140	-	0.91771	17716.0	0.91771	0.91771	17716.0	17716.0	177160	177160	172100
5	0	٥	2	2	٥	0	0	0	-	-	0	0	0	-	-	
C,	-	2	4	4	2	7	_	-	-		,	,	,		,	
ű	1	0	0	٥	٥	٥	2	m	,	-	,	,	,	,	7	7
ر.ً"	0.75	-	0.5	0.5	2.0	20	2	0.75	27.0	27.0	, [. ا	٥	o	0
·	<u>-</u>	-	-	-	-	-		-	-] -	3	3	5.0	S	0.5	0.5
V, (eV)	-35.12015	-30.19634	-112,61934	-111 25473	-38 24008	-36 88448	78 777 10	00000	307.7	-	-	-	-	-	_	
V, (eV)	12.87680	9.50874	73.95107		10.40706	20,000	40.11119	-107.32728	-/0.41423	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
7 (cV)	10.48587	7 27/22	10157.00	100000	10.40705	10.27417	23.03446	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
V (cV)	10076 5	31797	10,000	44.02081	11.18033	10.51650	29.77286	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
E(n m) (eV)	14 63480	2,00710	21.81193	04014-17-	-5.59527	-5.25825	-14.8B643	-16.26957	-10.53337	-5,24291.	-3.38752	-3,38732	-3.45250	-3.38732	-3.45250	-3.45250
Af: (2, 12)	10.00	4970741-		٥	-14.63489	-14,63489	-[4,53414	-15.56407	-15.\$6407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15 35946	-18 35946
1. Land to the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the sta	٥	0	-3.58557	-2.69893	-5,23932	4.35268	-1.65376	0	0	0	0	0	0		•	0
(and from on the	-14.63489	-14.63489	3.58557	2.69893	-9.39557	-10.28221	-12.88038	-15.56407	-15.56407	-14.63489	-15.56407	-15 56407	-15 350dK	EUrys SI	16 20046	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
(45) km m m;	•	٥	0	0	0	0	-14.53414	٥		6	6	6)OLOTO	2132340	13.33946
6y (n,sm) (eV)	-31.65533	-31.63534	-63.27075	-63.27074	-31.63533	-31,63537	-48.73668	-67.69451	-49.66493	-31.63553	-31 63537	31 61637	21 53636	2	0	0
$E_r(alom - alom, msp', AO)$ (cV)	0	-1.85836	-3,58557	-2.69893	-1.65376	-1.65376	0	•	6	•	7:858.I-	76660	21,00335	15050.10-	-51.63535	
E_ (10) (eV)	-31.63537	-53,49373	-66,85630	-65.96966	-33,28912	-33,28912	48 73660	0540479	40 66407	31,63	OCOCO-1-	1.03030	-1.449IS	-1.83836	-1.44915	-1.44915
ω (1011 rad / y)	24.1759	14.1117	60.9381	59.4034	13.0822	12 SR74	20 4067	74 020	24 346	10000115	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
Er (uV)	15.01299	9,28860	40.12366	39 1003 A	8 61003	9 19 576	20,000	27.7200	16/7:47	74.1739	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
E, (dV)	-0.24966	-0.20195	-0.41891	-0.40804	3/2010	0758770	39.1020	10.40840	15.97831	15.91299	6,21159	6.21159	10.19220	621129	6.29021	6.29021
E (cV)	0.35532					10.10337	021467	20.23.0	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
	(Eq. (13.458))	(18)	0.21747 [32]	0.21077	0.17358	0.17358	0.40929	(Eq.	0.35532 (Eq.	0.35532 (Eq.	0.12312	0.17978	0.09944	\$1221.0	0.12312	0.12312
E_, (cV)	-0.07200	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.18672	232220	0.14507	0 0 2000	03-01-0		2	ε	3	2
F., (aV)	0.14803	0.14803	0.11441	0.11441	0.14803	0 14803	0.14195	0 14800	2007.10	20,0,200	-0.10339	-0.0720	-0.15924	-0.10359	-0.10260	-0.10260
E, tum (eV)	-31.70737	-33,62241	-67.47664	-66.57408	27 10550	23 30 100	4011000	20000	0.14003	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
E (c, 10.10) (cV)	-14.63489	-14.63489	-14.63489	-14.63489	-14 67489	-14 63480	7176371	10776.10	49.80990	-51.70737	-35,59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (4. 20 no) (cV)	-13.59844		0	0	0	-	13 50844	12 60944	19.03489	-14,03469	-14.65489	14.63489	-14.63489	-14,63489	-14.63489	-14.63489
F, (damp) (eV)	3,47404	4,35263	8.70826	7 80660	4 12581	, 13313	10000	20000	-13.39844	-13.59844	0	0	c	0	0	0
					1977	7.1551.5	106/67/	1249180	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3 91734

Relative Error 0.00044 0.00035 0.00034 0.00034 0.00034 0.00034 0.00034 Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

Femands
Name
C - H (i) C - (ii) C - (iii) C - (iii)

Ed.	000000000000000000000000000000000000000
- 1	Energy (eV) 13,697 35,103 48,254 60,449 72,481 72,481
Calculated Total Bond	6.15222 11.68712 16.15222 41.305)22 60.40762 60.51509 72.68223
0-0	•••••
(e) 2-2	000000
(p) 2-2	9999699
C-C (c)	00000mo
C-C (b)	000000
C-C (a)	00-40-0-
CH (ii)	coc-000
CH,	F0367-40
, CH	0
(ii) NH ₁	
(i) C-N (ii) P Group	
(ii) C-N(i)	
(i) C=O (ii)	0
(C) C=O()	
Group Group	
_	- 5 6 6 6 6 6
	Formenide Actionide Proposanide Businanide Businanide E-Mediylopanenide Fertiananide Z-Dimethylopanenide Catananide Cottonnide
	CHIND FORMER CHIND Bearer CHIND Bearer CHIND Bearer CHIND Bearer CHIND Perena
İ	55555555

	Exp. 8			119.2 (formanide)			125.0 (formamide)	(sectamide)		122.0 (acetamide)	107 (propane)	(propand) (13.8 (butand) 110.8 (sebusard)	0 (butane) 4 (teobutane)	101.5 (nectore)			110.8 (isobutane)		(indestant)	(isobutane)	
	Cal. θ	-	108.27	118.61	119.04	116.18	124.91	116.63	124.63	56.121	103.44	110.49	110,49	109.50	109.44	109.44	110,67	110.76	111.27	111.27	107.50
	(o) 10																				
	6 C	,																			_
	Θ, <u>©</u>											. 69.51	15'69		70,56	70.56					250
	E, (cV)		0	0	0	c	-1.44915	-1,41915	1.63376	-1,44915	0			o			-1.85836		0	-1.83836	
m.msp' AO	ş		1.06R23	0.98033	1.02006	0.53052	0,83596	0.88749	0.83472	0.83596	1.15796			9625171			0.81549	1.04887	1.04187	1.04887	
aion - ato	ű		67.0	67.0	0.75	6,75	1	1	1	-	5 <i>L</i> D			0.75			-	0.75	0.75	0.73	
d. E. is E,	ហ		1	1	1	1	1	1	1	-	1			-			-	-		-	
de were use	r,		-	82.0	0,75	87.0	1	1	1	-	1			ı			1	67.0	0.75	0.75	
preceding an	C. Alpm 2		1	17716.0	0.93613 (Eq. (15 62))	0.83395 (Eq. (15.114))	N202N	0.91 M0 (Eq. (15.116))	0.85395 (Eq. (15.114))	0.83078	1			1			0181240	0.91771	12216'0	12216'0	
neters from the	ي آ		0.93613 Eq. (15.621)	0,93613 (Eq. (15.62))	0.91771	0.91771	0.84115	ณะสรรภ	a 81549	0.84115	0,86359			Q,RG359			0,81540	0,87495	0,87495	0,87495	
ion of θ , the paran	Atom 2 Hybridization Designation	(Table 15.3.A)	z	-	2	0	21	Z	0	11	Ξ			×			25	-		1	
the calculati	f. Crass		æ	ر <i>32573</i> ر	-14.53414 N	-13,61906	-16.37720 N	.14.33414 - N	20819'61-	14,37720 N	×	•		x			2) 2192931-	- 4.82575 (',	-14,82575 ر"	-14.82575 (' _e	
ntal values [1]. In	Atom I Hybridization Desturation	(Teble 15.3.A)	Z	72.	_	-	11	,	57	t)	,	i		,			St.	~	•	۶	
and experime	Ernstante Atem 1		-14,53414	N N	-14.X2575 (",	-14,x2573 C	16,17321 C)	-15.75493	11489'91-	16.17521 O .	-13,75403			-15.75-03			*,) ₹11±0'911-	.15.3503 .7	*,) stass's1-	*,) £205 5 51-	
lkyl amides	Zr. Terminal	Years (Cli)	3, 1464	3,9328	4.0825	3.723Ж	43359.	¥,6904	4.3607	¥167	3,4232			3,435			4,7958	4.1633	4,1633	4,7958	
aneters of a	2¢'	("")	1.94130	1.94130	261473	ugu	261473	264835	227954	2,64155	711106			1,11971.1			251547	2.11323	2.09711	2.90327	
id angle para	2c' Bend I	(°	1.94130	2.61473	2,162	2,11323	12272.1	2,86175	2.86173	1,27454	2,11106			111607			2.91547	2.91547	2.91547	2.90327	
Table 15.116. The band sugle parameters of alkyt surides and experimental values [1]. In the calculation of θ , the parameters from the preceding sugle were used. Fr is $E_r(atom - atom, m.p^2 MO)$	Almen of Angle		ZHNH.	(CH (i); C, =0 (i)	ZHC,N (CH (i); C, =0 (i))	ZHC,0,	ZOC_N (C, =0 (i))	\(\alpha', \C, N\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	(i) 0="5) 0".5".0	$\angle OC_{,N}$ ($C_{,n} = O$ (ii))	H".)H7	35.5.37	H'5'.77	H" THZ	7'.1'.77	н'.Г.77	به ر. ترکرگر	H, T, T,	H'.5'.)7	7,7 UM 77,17,17,1	'.Σ'.Σ'.

, 40).

N-ALKYL AND N,N-DIALKYL-AMIDES ($C_n H_{2n+1} NO, n = 2,3,4,5...\infty$)

The N-alkyl and N,N-dialkyl amides, $C_n H_{2n+1} NO$, comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C - C(O), is also a functional group. Formamide has a HC = O moiety that comprises a more stable C = O functional group and a 5 CH functional group that is equivalent to that of the iso-CH group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a $C - N(R_1)R_2$ moiety that comprises two types of C - N functional groups, one for formamide and the other for alkyl amides $(RC(O)N(R_1)R_2)$ where R is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a 10 single methyl or alkyl substitution, the NH - C bond and NH are functional groups, and the N - C bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. 15 The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The NH functional group was solved in the Hydrogen Nitride (NH) section except that the energy of the N-H MO is matched to the nitrogen-atom contribution to $\Delta E_{H_1,MO}(AO(HO))$ and $E_T(atom-atom,msp^3.AO)$ of the C-N group. The C-C(O) group, both N-alkyl or N,N-dialkyl amide C=O groups, and both C-N groups are equivalent to those given in the 25 Amides section.

As in the case of primary amines, each N-C group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

N-C H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.52) for the N-C-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ N)=0.91140$.

 $E_r(atom-atom, msp^3.AO)$ of the N-substituted amide C-C(O) group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, $-1.85836 \, eV$, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes, $C_{1o}=2C_1$ in Eq. (15.52).

 $E_{\tau}(alom-atom, msp^3.AO)$ (Eq. (15.52)) of the C=O group of N-substituted alky amides and the C=O group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the 10 Carboxylic Acids section are -2.69893~eV and -3.58557~eV, respectively.

 $E_T(atom-atom,msp^3.AO)$ of both C-N functional groups are the same as those of the corresponding groups of amides, $-1.65376 \, eV$. $E_T(atom-atom,msp^3.AO)$ of the singly-substituted NH-C-bond MO in Eq. (15.52) due to the charge donation from the N and C atoms to the MO is $-0.92918 \, eV$. It is equivalent to that of tertiary amines and matches the energy of the NH-C group to that of the C-N group wherein $E_T(atom-atom,msp^3.AO)$ of the latter is a linear combination of $-0.92918 \, eV$ (Eq. (14.513)) and $-0.72457 \, eV$ (Eq. (14.151)). $E_T(atom-atom,msp^3.AO)$ of the doubly-substituted N-C-bond MO is $-0.72457 \, eV$. It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the N-C group to that of the C-N group by matching one of the 20 components of $E_T(atom-atom,msp^3.AO)$ of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each $E_D(crossports)$ of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

of in-aikyi and in, in-dialkyi allildes.
Group Symbol
C-C(O)
C = O (i)
C = O (ii)
C-N(i)
C-N (ii)
NH
N-C (i)
N-C (ii)
$C-H\left(CH_{3}\right)$
$C-H(CH_2)$
C-H
C-C (a)
C-C (b)
C-C (c)
C-C (d)
C-C (e)
C-C (f)

Table 15.111	5. The geometri	Table 15.118. The geometrical bond parameters of N-alkyl and N.	ters of N-alleyl a	nd N.N. dialkyl	N-dialityl amides and experimental values [1]	rimental values	(1)										
Parameter	(0),3-,2	(I) O=2	(ii) (ii)	C-N (i)	C-N (ii)	HN	(i) 2-N	(ii) 2-1/	N-C (ii) C-H (CH.) C-H (CH.)	C-H (CH.)	H-3	(8))	(9) .))	(c-C (c)	(p)	(0) .)-2	ن-ن (و
-	Group	dage	Group	Group	Group	Group	Group	Group		- -	Group	Group	Group	Group	Group	Group	Group
						.			Group	Group							
a (a.)	2.04740	1.290799	1.29907	1.70920	1.75370	1.28620	1.96313	1.97794	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2,10725	2,10725
0, (0,)	1.43087	1,13613	1.13977	1,30736	1.32427	90756.0	1,40112	1.40639	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 1c' (A)	1.51437	1,20243	1.20628	1.38365	1.40155	1.01291	1,48288	1,48846	1,10974	(11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53655	1.53635
Exp. Bond	025		\$27.1		!		1469		1.107 (C-H	1.107 (C - H	:	1.532	1.532	1.532	1.532	1.532	1.532
Length (Self)	(N-methyl-	(formamide)	(N-maleri-	(formamide)	(acctamide)		(N-methyl-		propane)	1.117	(isobutane)	(propane)	(propane)	(propane)	(propane)	(propane)	(propane) 1.531
			Ì						(C-H butane)	(C - H butane)		(butane)	(butane)	(butane)	(butane)	(butane)	(butene)
b.c (a.)	1.46439	0.61267	0.62331	1,10098	1.14968	0.85927	1,37505	6,39079	1.27295	1.29569	1.29924	1.54616	1,54616	1.52750	1.54616	1.52750	1.52750
٠	0.69897	0.88018	0.87737	0.76490	0,75513	0.74410	0,71372	0.71104	0.63580	0,63159	0.63095	00989'0	0.68600	0.68888	0.68600	0.68888	0,68888

Table 13.119. The MO to no intercept geometrical parameters of reserving and representations are 7.1 them. 9. decay.	בנונישו החווה	parameter s or	and I was												
Band	Alom	ائم (eV) Bond ا	E, (eV) Bond 2	(cV) Bond 3	رج (eV) Bond 4	Find Total Energy (*2yr) (eV)	<u>) </u>	ું હ	(eV)	E(C.24v') (eV) Final	e ©	6 0	e,€	(a) (a)	(a, c,
$H \subset_{\mathcal{L}}(U) \times (C_{\mathcal{L}} \times) - H$ $(C \cong O \ (i) \text{ and } (i))$ $(C \subseteq N \ (i) \text{ and } (i))$	N	-n x2/xx	.n 46459	u			0,03084	U\$4218	-16.11723		11547	RE 53	67.03	0,59403	0,36363
$RC_{a}(0)N(H) - C_{a}H_{b}$ (C = 0 (i) and (ii)) (C - N (i) and (ii)) (N - C (i))	2	-41 KZJAJOK	40 464 59	c	e		nanic o	al reel in	:16.11713		78.61	£ 10	. 107/4	1.56779	0 16667
$KC_{\mu}(0)N(H) - C_{\mu}N_{\mu}$ ($C = 0$ () and (ii)) ($N - C$ (i))	من	05 17% 0-	e	¢	c	-152,04028	0.91771	បរខន្ធវាប	-15.00t.21-	-15.09948	K1.37	26.63	D) (r)	1.50383	å. (027)
RC_(O)W(H)-C,H,C,H,R (C=O () and (ii) (C-W () and (ii)) (N-C (i))	2	NO KOLONGY	astur o-	ė			0,970964	0,84418	16.1172		78.61	UE 101	37 (0	1.56779	0.16667
RC_(Cr)N(H)-C_4H_1C_HR (C = O (1) and (il)) (C = N (1) and (ii)) (N=C (i))	ڻ	(SH)P OF	H1626 B-	u	e	94WD181-	1440	11,83,885	-16 21952	-14.02866	78.02	101.39	3664	ነ. የ	0 17413
ルで、(の)N(C,H,)ーC,H, (C=O (f) and (f)) (C=N (f) and (fi)) (A-C (fi))	₹.	NOTA IT	מיבאי ה.	436279	e		0.9%944	O.H3473	-16 377 <u>20</u>		75.57	104.43	38.35	901978	0.20697
##C_(O)#\{C,H,}=C,H_1 (C = O () and (ii)} (C = H () and (ii)} (H = C (ii)	C.	atom.	e	v	. :	-151.9779R	0.91771	0.89582	-15.18004	-14.99317	. кд.59	9741	D7.KC	1.52188	\$11549
$RC_{c}(r)N(C,H,C_{c}H,N)-C_{c}H,$ (C=O,(1) and (0)) (C-N,(1) and (0)) (N-C,(1))	И	MANUTA IT	40 36229	attyr'u-	B		a 93 uts	0.83078	0.05772301-		75.57	104.43	35.35	1.61336	0.200697
$RC_{a}(r)N(C_{a}H_{1}C_{a}H_{1}R)-C_{a}H_{2}$ $\{C=O_{1}(t) \operatorname{and}(t)\}$ $\{C-N_{1}(t) \operatorname{and}(t)\}$ $\{N-C_{2}(t)\}$	ر.	6723515	c	e	3	4(51.9779R	17719.0	18208.0	-15,18804	-14.90717	82.59	97.41	39.70	1.52188	011349
$R \subset (H)N(R') - C_{\mu}H_{\nu}C_{\mu}H_{\nu}$ $(C = O \ (i) \text{ and } (ii))$ $(C - N \ (i) \text{ and } (ii))$ $(N - C \ (ii))$. N	41 K3/54K	מבאנט	617870	. a		P\$05670	0 RWTR	02772.01-		73.57	104.43	35.35	1.61336	7697£ 0
PC,(Ω)V(R)−C,H,C,H,R (C = O (t) and (ii)) (C − N (t) and (ii)) (N − C (ti))	ú	んごとりといっ	жыст	D.	c	-152.90716	0.917TE	UPMIR	-16.11722	-15.222.36	17.11	10.11	36.28	1.59451	0 (8812
$HG_{\omega}(0) - N(H)R$ (C = O(0)) (V = U(0)) (V = C(0)) R = methyl or altyl	×	-ri #265#	41 464.59	E	U		13084 U	0.84418	.16,1172		102.07	77.93	457	1.15050	0 176.17
$HC_{\mu}(\Omega) - N(H)R$ (C = O, 0) (C = C N(1)) (N - C, (0)) R = inethyl or alkel	7	47.92.688	-1.79278	U	c	5124451-	0 91 77 1	0.77501	11544,71-	-17.25455	36.81	83 19	44.70	1,21492	HEE0 0
$HC_{\alpha}(\Omega) - N(R)R$ $(C = \Omega)$ $(C = R)$ $(C = R)$ $(R = R)$ $(R = R)$ $(R = R)$ $(R = R)$	N	-0, H2GK C	6229811-	4136119	O		48055°0	Q.83078	02772.01-		101.03	78.97	67.79	1,14542	0 15895
HC,(O) - N(R')R (C = O (i)) (C - N (i)) (N - C (ii))	٠,٠	.0 K2688	мттет.	0	0	-154,23533	0 91771	16677.00	17.4451	-17.25455	38 38	K3.19	06.84	26P12-1	0.00244

R. H. waeting or olkyl	L														
$R: H_{\mathcal{C}, C_{\mathcal{C}}}(\Omega) - N(H)R$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O(11)$ $C = O$	2	887,X X UT	05178°U-	c	c		נימומרו	0 842318			98.16	12.12	29 97	1.3046	0.11962
(C = O(1)) (C = O(1)) (N - C(1)) (R = REHIM or alky)	۲,	ARZAR.	ማሴተ ' ነ-	41.92918	c	15157.421	ונדופה	0.75878	-17,93127	17,74041	20.51	89.49	4130	1,317.55	0.00672
$R^{-1}(G) = N(R)R$ $(C = O(R))$ $(C = V(R))$ $(N = C(R))$ $(N = C(R))$ $(N = R)$ $(N = R)$	2	A),R),A	672X 0-	470779	0		ተመሂሉህ	87078 0	-16.3772.0		77.06	87.98	45 82	02277	0.10207
	ن	אאטלא מ-	0.1.342A6	\$1676 G	, o ·	18473131	1/21/2V	N.7547H	721/0271-	187221-	15'06	57'64	71.30	131755	0,00073
$RC_{n}(N(R) C) = O$ C = O (1) $RC_{n} = H$ unches, or alter H : $(N(R) D) = O$	2	NTEUT.I.	٠	С	a ·		l,mera	0.8187	-16.61.833		137.10	75.00	65.45	0.53635	Q.5997.R
(C=0,(R)/R)=R (C=0,(R)/R)=R (C=0,(R)/R)=R (C=0,(R)/R)=R	ن ا	ятачт.	TI NEWSKI	с	•	-15423535	17716.0	12957.0	117,4831	-17.25.85	135.44	44.56	អ្	0,58044	11.55569
(C = O(1)) $R(R) = O(1)$ $R(R) = O(1)$ $R(R) = O(1)$ $R(R) = O(1)$ $R(R) = O(1)$ $R(R) = O(1)$ $R(R) = O(1)$	a	9161[]	c				п. Эжоо	SILMED	-16.17521		137.27	42,73	6631	0.52193	0.61784
(C=0) (f) (n n n n n n n n n n	ن	98681-	HISCHI)-	4162214	· ·	15472121	0.91771	8782F.C	-17.93127	1404771-	133.07	4633	61.70	061582	0.52395
$H = ((O) \cap (H^*) K$ $H : H^* = H$, methyl, or alkyl $BH : (-c^*(O) \times (D^*) C$:	ж267.1-	4882688	=	c	-154,23535	0,91771	16677.0	17,44541	-17.25455	60.9	113.61	32.13	1,41810	0.36148
R.R" = H. methyl, or othyl H.C C (0)N(H)P	ر.	41 927 IK	Altern.	10 X X 20 K	8	-154,72121	11110	0 75K7R	7218971-	-(7.7406)	zurs	122.98	33.76	1.84386	0.41299
R.R" = H. mellyl, or alkyl RH, C.H, C, - C, (1) N(R") R	ان	XI6E&Ir		8	a .	152.54407	177160	0.80399	-15,75493	-15.56407	ונת	107.73	E.M.	1.693KB	100,000
R.R. a.H. methyl. or othyl. CH (CH.)	ن ا	XICEGO-	HIGGGIF	а	e	-153,47405	17116.0	0.81547	-16.68411	16 49125	(6.93	11401	30.58	1.76770	DIECO
C-H (CH,)		SIGGO	o later	e :	ء ا	-152.54487	17LIGU	0.85359	-15,75.03	.15.56407	77.49	is di	41.48	1,2364	0.187DR
C-H (CH) (II)		NICEGO.	NICEGO-	\$1046 G.		153,47406	กอเกา	0 KI 519	-16,64412	-16.4923	68.47	111,53	35.84	1,75486	0.29933
H,C,C,H,CH, (C, -(', (a))	ن	MIGEG.O.		o		-152 54487	12121	0.86359	-15 75493	15,56407	01.16 5X.53	116.18	31.37	1,42588	35572.0
H.CC. (a))	j.	*1020.0-	40.0201K	c	e	. (51.474ms	17716.0	0.81549	-16 (8412	-16.49323	- X8	13.59	30.5%	1.90800	0.45117
$R = H_1(C_n^*(H_1C_n - R^n)H(H_1 - (C_n - C_n)H(H_1	٠	402018	48.9291x	N1676 tr	u	154,40324	177100	4,772,47	-17.61330	-17,42244	£, 30	51.70	21,90	1.97162	0.513#8
$\frac{(G-C,G)}{(G-C,G)} = \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2$	ت	# Jegg o	-0.72457	12457.0-	472437	.154,71860	14716.0	0.75889	-17.92%66	647.57.71	# 21	67.181	21.74	1.95734	0.505.0
(C=C, (d))	· *	A1029.0-	4.02918	419291k	5	-1\$4.4033-	1,7119.0	נידננס	-17.61330	17,42244	48.30	07.12t	21.30	1,97162	Q.5138R
$((1-(1-1)^2)^2)^4 (4-1)^2 (1)^2 - (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)^2)^2 (1-(1-1)$	٠٠	12,17,13,57	4,71457	417157	ופענה	-154.51399	17710.0	0 16765	17.92866	677.71.	\$0,04	129.26	27.00	1.94462	0.49208
(C-C (D) (C-C (D) (W-H.C)C (R-H.C)CH =		477487	A19291A	4192914	ė	-134.17803	17712 0	551×C0	-17.40%9	-17.21783	52.78	27.23	80 72	1.92413	0.47279
(C-C (0)	ئ	4173457	4172457	7,72457	-0.73457	-154.51399	122120	0.7676.5	-17.91KG	617.771-	30.04	129.96	37.00	1.94462	0.49298
										i					

		֡															
	Group	Group	Group	Group	Group	Group	N-C()	N ~ C (ii)	Group	Group	G g	Grand	Gond	Graup	Grade	Og e	Gan
M	-	2	2	-	-	-	_		3	2	_	_	-	-	-	-	-
u,	٥	٥	0	0	0	0	0	0	2	-		0		٥		•	-
п,	٥	°	0	٥	0	0	0	0	٥	0	٥	٥		٥	۰	٥	0
	20	0.5	0.5	0.5	2,0	0.75	20	2	27.0	0.75	0.75	20	20	2	2	25	S
	-	_	-	_	-	0.93613	-	-	-	-	_	-	-	-	-	-	-
<i>c</i> ₁	_	-	-	-	-	0.75	-	-	-	_		-	_	-	-	-	
້ະ	12216'0	0.85395	\$6538.0	0.91140	0.91140	-	0.91140	0,91140	0.91771	17716.0	177160	17716.0	17716.0	17716.0	17716.0	17716.0	0.91771
c,	٥	7	7	0	0	-		0	٥	-	-	٥	0	0	-	-	0
6,	2	4	Þ	2	2	1	2	τ	-	-	-	2	1	2	2	2	7
<i>c</i> ,	0	0	0	0	0	-	0	٥	3	2	_	0	0	0	0	۰	0
	-	0.5	5.0	0.5	0.5	0.75	0.5	5'0	0.75	0.75	0.75	2	0.5	2	ຣ	2.0	2
	-	-	-	-	_		-	_	~	-		-	_	-	-	-	-
1, (et')	-30.19634	-112.61934	-111.25473	-38.24008	-36.88558	-40.92593	-31.67393	-31,36351	-107.32728	-70,41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
f, (el')	9,50874	70156.62	13.87467	10,40705	10,27417	14.21618	9.71067	9.67426	38.92728	25.78002	12.87680	9.33352	9.3332	9,37273	933352	9.37273	67575.9
T (eV)	7,37432	43.62380	42,52081	11.18655	10,51650	15.90963	8.06719	7.92833	32.53914	21.06675	10.48582	6.77464	6.77454	6.90500	6.77464	6.90500	6.90500
i. (et')	-3.68716	-21.81195	-21.41040	-5.59327	-5.15825	7.95482	4.03339	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
Elwind (el.) .	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-14.63489	-14,63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-1535946	-15.35946
DEnization m) (et)	0	-3.58557	-2 69893	-5 23932	4,35368	-1.65376	-0.92918	-0.72457	0	٥	٥	0	0	0	0	0	0
E, Inn well (eff.)	-14.63489	3.58557	2,69893	-9.39557	-10,28221	-12.88038	-13.70571	-13.91032	-15.56407	-15.56407	-14.63489	-15,56407	15.56407	-15.35946	-15.56407	-15,35946	-1535946
F, lupul (ei')	-31.63534	-63,27075	-63.27074	-31,63533	-31,63537	31,63531	-31.63537	-31,63540	-67.69451	49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	31,63535
$E_T(atom - atom, m.gr', AO)$ (c1')	-1.85836	-3.58557	-2,69893	-1,653.76	-1.65376	0	-0.92918	-0.72457	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1,44915	-1.44915
f, lun (el')	-33.49375	-66.85630	-65.96966	-33,28912	-33,28912	-31.63537	.32.56455	-32,35994	-67.69450	49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
(s) rad/s)	14.1117	60.9581	59.4034	13.0822	12.5874	44.0494	8729.01	10.5087	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
Eg. (eb.)	9,28860	40.12366	39.10034	8.61093	8.28526	29.58649	6 99543	6,91703	16.40846	15.97831	15,91299	6,21159	6.21159	10.19220	621159	629021	6.29021
E., (el)	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.34043	-0.17039	-0.16837	-0.25352	-0.25017	-0.24966	-0.16315	-0.16515	-0.20896	-0.16515	-0.15416	-0.16416
E _{tob} (ef')	0.14655 (28)	0.21747	0.21077 [21]	(tt)	0.17358 [33]	0.40696	0.12944	0 12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.3532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312 (2)	0.12312	0.12512 [2]
E, (cf.)	-0.12867	-0.31017	992050-	-0.10647	-0.10278	-0.13695	-0.10567	-0.10365	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (c//)	0.14803	0,11441	0.11441	0.14803	E0844.0	.0.14185	0.14803	0.14803	0,14803	0.14503	0.14503	0.14803	0.14803	0.14803	0.14803	0.14803	0,14203
E, to - (cf.)	-33.62241	-67.47664	16725'99	-13,39559	13,39190	-31.77232	-32.67022	-32,46359	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
F (61. 10 10)	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.53414	-14,63489	-14 63480	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489
Empels. wm (eV)	0	0	0	0	٥	-13.59844	o	0	-13.59844	.13.59144	-13.59844	0	0	0	0	0	0
E. (rung) (c.F.)	4.35263	8.70826	7.80660	4.12581	4,12212	3,49788	3,40044	3.19381	12.49186	7.83016	3 32601	4 12754	4.29921	3 97398	4.17051	82129	3.91734

Altered Arghe 75. 7. 7. 1. Altern 1. Attent 2. 1. Attent 2. 1. 1. Attent 2. 1. 1. Attent 2. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.	1,2	1,,,	,,'	,,	Atom	1	Atom 2				,			1	,	,	Т	100	
	1	land)	Tonsinst	New C	Hybridezetion Designation	Crimback Alpes 3	Hybridization Designation	C. Termin	V V	5		ۍ :	v.	ey 4	ø, €	æ⁻ €	e. ©		exp.
					(Teble 15.3.A)		(Table 15.3.A)	 				•			 	 :		 ;	
$\mathcal{L}C_{n}^{\prime}N$ $(C_{n}^{\prime}=O_{n}^{\prime}(i))$	2,27954	2,64835	43243	0	13	-16.11722 N	п	0.84115	0.84418	-	-	-	0.84266	-1,44915				12.231	121.8 (N-methylacetamida)
(C, = 0 (ii)	2.86175	2.64835	4.6904	-15.75493 C.	7	-14.53414 N	z	0.86339	0.91140 (Zq. (15.116))	_	-	-	0.88749	-1.44915				116.63	114.1 (N-methylacetamide)
ZC,C,O (C, = 0 (ii))	2.86175	2.27954	4.5607	-16.68411	72	-13.61806	o	0.81549	0.85395 (Eq. (15.114))	_	-	-	0.83472	-1.65376				124.63	
$\angle C$; NC , $(C_n = O \text{ (ii)})$	1.64833	2.80224	4.6904	-(793127 C,	\$	-16.219 52 C,	41	87857.0	0.83885	-	-	-	0.79881	-1.83836				118.72	119.7 (N-methylacetamide)
Methiton ZHC, H	711106	2.11106	3.4252	-15.75493	,	Ξ	н	0.86339	-	-	-	0.75	1.15796	0				108.44	107 (propane)
לנ'פ'נ'															69.51			110.49	112 (puratoria) 113.8 (butane) 110.8
H"5"57								i	·						1569			110.49	(buttene) (factorie)
H":)H7	2.09711	11760.5	3,4252	-15.75493	7	æ	x	0.86159	-	-	-	0.75	1.15796	0		-	-	08.60	108.5 (acetone)
ZC,C,C,															70.56	-		109.44	
4C,C,H															70.56	-	-	109.44	
∡ς,ς,ς, ⊪.ς,	2.91547	2,91547	4.7958	.16,68412 C.	57	-16.58412 C,	25	0.81349	0.81549	-	-	-	0.81549	-1.85836			-	110.67	110.8 (Eobutane)
. ZC,C,H C,	2.91547	2,11323	4.1633	-15.55033 C,	~	-14.82575 C ₂ :	_	0.87495	177160	0.73	-	6.70	1.04887	۰			\dagger	110.76	
ДС,С,Н ъ. С,	1.91547	112607	4,1633	-15.55033 C _b	s	-14.82575 C.		0.87495	17716.0	87.0	-	6.7.0	1.04687	0			_	111.27	11f.4 (isobutane)
2C,C,C, سرح,	72,90327	2,90327	4.7958	.13.55033 C.	8 1	-14.82575 C,	_	0.87495	0,91771	67.0	-	67.0	1.04887	-1.85836		-		11.27	111.4 (Isobumne)
ZC,C,C,															200	1	f	1	

UREA (CH_N,O)

Urea, CH_4N_2O , comprises a C=O functional group and two $C-NH_2$ moieties that each comprise a NH_2 functional group and a C-N functional group. The C=O group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The NH_2 and C-N functional groups are also equivalent to those given in the Amides section. E_T (atom-atom, msp³.AO) (Eq. (15.52)) of the C=O and C-N groups are equivalent to those of formamide. The values given in the Amides section are $-3.58557 \, eV$, and $-1.65376 \, eV$, respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Functional Group	Group Symbol
C=O (urea)	C = O
(O)C-N (urea)	C-N
NH₂ group	NH_2

(a) "c"

_		_,	~- - -		···			7
	NH,	Group	1,32297	0.97065	1.02729	1.027 (formamide) 1.022 (neetamide)	0.89894	0,73309
and experimental values [1].	N-2	Group	1.70920	1.30736	1.38365	1.368 (fornamide)	1,10098	0.76490
To No. 14 104. The neometrical band parameters of orce and experimental values [1]	000	Group	1.290799	1.13613	1,20243	1.212 (formamide)	0.61267	0.88018
Toble 15 174 The neum	Parameter		a (u,)	c' (a,	Bond Length	Exp. Bond Longib	h, c (u ₀)	

68	(C)	62.13		20.02		42.45	3737	250	61 27	
9		66.10		76,07		4 2	-	3,7	46.18	
,a	. C	9110	1				-	_	13.82	1
1	c(C.Z.pr) (e.V.) Final		-	_	+	18.08143	+	_	1808143	1
+			•	12	-	_	1	- -	-	+
1	19E		15.652	15.65		-18272	-	-16.618	9505.81	
	<u>1 </u>		0.86923	o Denn's	0.00769	0.74461		0,81871	1 ALLE	3
] &		0.93084	1	0.93084	124100		00000	0.0100	C'ALCO
	Final lotal Energy C2.p	(6)				100 000	133.00			155.00223
mor inc.	E, (eV) Bond 4		•		0		٠		2	0
7 (chin) - Onini.	Er (eV) Bond 3		•		0		-O. 1.2063		7	-0.62688
cond parameters of urea. Cr 18 Cr (umin continuent)	/5, (eV) Bond 2		·	,	•		-1.79278		0	0.82688
nd parameters o	<i>E_T</i> (eV) Bond (Page 6.0-	A STACE OF		0.82688		1.707.18	1, 79278
8	Акош			2	,	٤	٠.		0	٠
Table 15, 125. The MO to HO intercept geometi	pu			1.NC(O)N(H)-H	11000	M,NC(U) - NM,	NCON-NW	mc(0) - (11)	H,NC,(NH,)=0	U ANT CAUM I = O

Table 15.126. The energy parameters (eV) of functional groups of urea-

Parameters	C = O	C - N	NH ₂
	Group	Group	Group
n _i	2	1	2
n_1	00	0	0
<i>n</i> ₃	0	0	1
<i>C</i> ₁	0.5	0.5	0.75
C,	1	1	0.93613
c,	1	1	0.75
<i>c</i> ₂	0.85395	0.91140	1
c_3	2	0	0
<i>c</i> ,	4	2	1
c,	0	0	2
C _{lu}	0.5	0.5	1.5
C _{2"}	ı	1	1
V. (eV)	-112.61934	-38.24008	-78.77719
$V_{p}(eV)$	23.95107	10.40705	28.03446
T(eV)	43.62389	11.18655	29.77286
$V_m(eV)$	-21.81195	-5.59327	-14,88643
E(MOIHO) (eV)	0	-14.63489	-14.53414
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-3.58557	-5.23932	-1.65376
$E_{T}(AOIHO)$ (eV)	3.58557	-9.39557	-12.88038
$E(s, \lambda O)HO)$ (eV)	0	0	-14.53414
$E_{\gamma}(H,MO)$ (eV)	-63.27075	-31.63533	-48.73668
$E_{\tau}(alom-alom, msp^3.AO)$ (eV)	-3.58557	-1.65376	0
$E_{r}(m)$ (eV)	-66.85630	-33.28912	-48.73660
$\omega \left(10^{15} rad / s\right)$	19.9334	13.0822	59.4067
E_{κ} (eV)	13.12053	8.61093	39.10250
\bar{E}_{D} (eV)	-0.23955	-0.19325	-0.39136
\bar{E}_{Krib} (eV)	0.21747 [32]	0.17358 [33]	0.40929 [22]
\vec{E}_{ox} (eV)	-0.13081	-0.10647	-0.18672
$E_{max}(eV)$	0.11441	0.14803	0.14185
$E_{\tau}(Gring)$ (eV)	-67.11793	-33.39559	-49.11003
Einstal (c. MOTHO) (eV)	-14.63489	-14.63489	-14.53414
Einmal (c. AOIHO) (eV)	0	0	-13.59844
$E_{\nu}(Group)$ (eV)	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

Formula	Name	C = O Group	C – N Group	NH ₂ Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH ₂ N ₂ O Urea		1	2	2	31,35919	31.393	0.00108

(atom - atom man AO)	
j. is 12.	•
7,, the parameters from the preceding angle were used. E	
alculation of $ heta$	
es [1]. In the c	
a and experimental valu	
Brameters of ure	-
and angle p	
l able 15.128. The bo	The state of

	Exp. θ (°)				561	(formamida)	
	(a) (b)			108 27		18.6	1
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	ø_ ⊙						
	ø, Œ						
	E _T (eV)		•			2	
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	ť		_		0,75		
,	C ₁ Atum 2		_		1221610		04040
	C ₂		0.93613	13.04	0.93613	(fame) ha)	211720
	Atom 2 Hybridization Designation	(1 nble (3.3.4)	x		-		-
	Abra 2		Ξ	-13 K2574		06221	
	Atom I Hybridization Designation	Trans 12.3.A)	z		z		7
	Altern 1		-14,53414	FIFTS FI-	2	16.17521	
	Tennius Noun (u,)		3.15		3.9328		667
	(a)		1,34130		813		C/MIG-7
-	(a)		1.74[3]		(/FIN7	*****	39.54
Appete of Age.		7010	- UNIV	NA	, , , , , , , , , , , , , , , , , , ,	N.JOZ	

CARBOXYLIC ACID HALIDES $(C_n H_{2n-1}OX, X = F, Cl, Br, I; n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acid halides, $C_nH_{2n-1}OX$, comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. All carboxylic acid halides further comprise a C-X functional group where X is a halogen 5 atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of 10 straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide C = O and C - C(O) groups are equivalent to those 15 given in the Aldehydes section and the Ketones section, respectively. The values of $E_T(atom-atom, msp^3.AO)$ given in these sections are $-2.69893 \, eV$ and $-1.44915 \, eV$, respectively.

As in the case of alkyl halides, each (O)C - X group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing 20 of electrons between the $C2sp^3$ HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the (O)C - Cl H_2 -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor C_2 of Eq. (15.52) for the (O)C - Cl-bond MO given by Eq. (15.111) is $C_2(C2sp^3HO\ to\ Cl) = 0.81317$. The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the C-Cl group of alkyl chlorides, $E_T(atom-atom,msp^3.AO)$ of the (O)C-Cl-bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the C and Cl atoms to the MO is $-1.44915 \, eV$ where both energy contributions

are given by Eq. (14.511). This matches the energy of the C - C(O) functional group with that of the (O)C - Cl group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs. 10 (15.79-15.108) are given in Table 15.134.

Table (5, 129, The [Functional Group. C-C(O) C-C(alkyl carbox (O)C-C! Eth. group CH, group CH, group CH group CC bend (n-C) CC bend (fen-C) CC bend (fen-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C) CC (iso to iso-C)	Table 15.129. The symbols of functional groups of alkyl cathoxylic functional Group C-C(0) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10) C-C(10)	(9)	C-H C-H C-H C-H C-H C-H C-H C-H C-H C-H	(CO) (CO) (C(CH, 1) (CH, 1) ((B) (B) (CO) (CO) (CO) (CO) (CO) (CO) (CO) (CO								
				[] Salley letternimery bus solinely bion	ental values [1].						1,20	9,00
Table 15,130 Parameter	Table 15.130. The geometrical band parameters of alkyl carboxylic parameter $C - C(O)$ $C = O$ $C - C$	C=0		C-H (CH,)	C-H (CH ₁)	C-H Group	C-C(a) Group	Group Group	C-C (e) Group	C-C (d) Group	Oroup	Group
	Croup	1000	167626	Group	Croup	1.67465	2.12499	2,12499	2.10725	2.12499	2.10725	2,10725
a (a _b)	2.04740	77951	1,69136	1.04856	1.05555	1,05661	1.45744	1.45744	1,45164	1.45744	1,45164	1,45164
Bond Length	1,51437	1,20628	1.79005	1.10974	1,11713	1.11827	1,54280	1.54280	1.53635	1.54280	1.53635	1,53635
3c. (A)	_						, 637	1 613	1 532	1.532	1.532	1.532
Exp. Bond	1,520 (acetone)	1.187 (acetyl chloride)	1.798	(.107 (C - H propane)	(C-H propane) (C-H propane)	1.122	(propane)	(propane)	(propane)	(propane)	(propane)	(propane 1.531
	1,518	1,214	(acetyl chloride)	1.117	1.117 (17 - 24 butane)	(Isobulare)	(butane)	(butane)	(butane)	(butane)	(butanc)	(butane)
	(2-butandne)	(acetic acid)	1 59705	1,27295	1,29569	1,29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
0'0 (no)	1,404.39	72772	0 77709	0.63580	0,63159	0,63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888
0	U.09667	0,01/0,	0.12.07									

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides. R,R,R' are H or alkyl groups. E_T is $E_T(alom-alom,mxp^2AO)$.

_	W() 2	200	07 —	/0:	510	078	3							6	50			
	(§)		0.30463	0.44625	0.61784	0.53901	0.39408	0.24675	0.18708	0.29933	0.37326	0.38106	0.45117	0.51388	0.50570	0.51388	0.49298	0.47279	0.49298
,	- (°)		1.99599	2.13760	0.52193	9.60076	1.82495	1.67762	1.23564	1.35486	1,42988	1.83879	1.90890	1,97162	1,95734	1.97162	1.9462	1,92443	1.94462
a	r©		30.00	22.23	66.31	62.45	26.96	34.98	41.48	35.84	31,37	30.08	26.06	21.90	21,74	21.90	32.66	24.04	22.66
8	· ©		110.38	125.31	42.73	45.72	120.70	106.38	102.51	111.53	118,90	116.18	123.59	131.70	131.79	131.70	129.96	. 127.22	129.96
.0	, ©		69.62	54.69	137.27	134.28	59,30	73.62	77.49	68.47	61.10	53.82	¥. 14.	48.30	48.21	48.30	\$0.04	52.78	8.8
(100)	(eV) Final			-17,43350		17,43350	-17,43350	.15.35946	-15.56407	16.49325	- 17.42244	-13.56407	-16,49325	-17.42244	-17,73779	-17,42244	977(7,7).	-17.21783	47.73.7.7
E	(eV) Final		-15.55033	-17.62436	-16.17521	17.62436	-17.62436	-15.55033	-15.75493	-16 68412	-17,61330	-15,75493	-16.68412	-17 61330	-17,92866	-17,61330 -	-17.92866	-17.40869	-17,92866
	(g)		0.87495	0.77199	0.84115	0.77199	0.77199	0.87495	0.86350	0.81549	0,77247	0.86359	0.81549	72577.0	0.75889	0,77247	0.76765	0.78155	0.76765
,) (°		1.05158	17716.0	1.00000	17716,0	0.91771	0.91771	17710	17710.0	0.9177।	17719,0	17110	17716.0	0.91771	0.91771	0.91771	17716.0	12216'0
Final Total	Energy C2sp ³	3		-154.41430		-154.41430	-154.41430	-152.34026	-152.54487	-153.47406	-154.40324	-152.54487	-153.47406	-154.40324	-154.71860	-154.40324	-154.51399	-154.19363	-154,51399
H	(eV) Bond 4		٥	0	٥	D	0	0	0	0	0	0	c	a	-0.72457	0	-0.72457	ó	-0.72457
, F	(eV) Bond 3			-0.72457	. 0	-0.72457	-0.72457	0	. 0	0	-0.92918	0	0	8 1626 0.	-0,72457	-0.92918	-0.72457	-0.92918	-0.72457
12	(eV) Bond 2			-0.72457	٥	-0.72457	-1.34946	0	0	-0.92918	-0.92918	0	-0.92018	-0,92918	-0.72457	-0 92918	-0.TJ457	-0.9291\$	-0.72457
F.	(eV) Bond I		-0.72457	-1,34946	-1.34946	-1.34946	-0.72457	-0.72457	-0.92918	-0.02918	-0.92918	-0.92918	8 (626 0-	-0,02918	-0 92918	-0 92918	-0,71457	-0,72457	-0.71457
Atom		1	3	ن	0	ີ່	ڙ	ť	Ü	t		ີ "	ڻ	ڻ	5)	ر.	ڻ	C,	້:
Bond		10 (0) 000	H.J.L. (U)CI	H,C,C,(0)-CI	$H_iC_kC_k(C_l)=0$	$H_{\lambda}C_{\lambda}C_{\lambda}(CI) = 0$	H,C, -C, (O)-CI	H,C, -C,(0)-Cl	$C-H$ (CH_3)	$C-H$ (CH_1)	C-H (CH) (ii)	$H_iC_{i,C_i}H_iCH_i - (C-C^{-1}(a))$	$H_iC_aC_iH_iCH_i$ – $(C-C_iC_iA)$	$R - H_2C_{*}C_{*}(H_3C_{*} - R^{2})HCH_3 - (C^{-}C_{*}(b))$	$R - H_3C_s(R^* - H_3C_s)C_{1s}(R^* - H_3C_s)C^*H_1 - C^*C_s(C)$	$I_{K^{\prime}}(C, L^{\prime}(H_{2}C, -R))HCH_{1} - (C, -C, (d))$	$tan(C_{\bullet}(R-H_{\bullet}C_{\bullet})C_{\bullet}(R-H_{\bullet}C_{\bullet})CH_{\bullet} - (C-C_{\bullet}(e))$	$IUMC_{s}(K_{1}(H_{1}C_{s}-R))HCH_{2}-(C-C_{1}(f))$	$knC_{\alpha}(R^{n}-H_{1}C_{\alpha})C_{\alpha}(R^{n}-H_{2}C_{\alpha})CH_{2}-$ $(C^{n}-C^{n}(\mathbb{D}))$

						****		1,000		11,00	1	9,00
Parameters	Group	Group Group	Group Group	Group	Crown	Group	Group	Group	Group	Group	George Group	Group
lu lu	_	2	-	3	2	-	-	-	-	-	1	-
n_2	0	0	. 0	2	-	0	0	0	0	0	0	0
The state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the s	0	o	0	0	0	0	0	0	0	0	0	0
ئ	0.5	0.5	0.5	. 0.75	0.75	0.75	0.5	0.5	0.5	20	0.5	0.5
ئ	-	_	0.81317	_	_	_	1	1	-	-	ı	
้	-	_	-	-	_	_	1	-	-	-		1
ধ	0.91771	0.85395	1	17710.0	17710	0.91771	17716.0	0.91771	0.91771	0.91771	0.91771	0.91771
ร์	0	2	-	0	1	1	0	0	0	-	1	0
°2	3	4	2		1	ı	2	2	2	2	2	2
5	0	0	0	3	2	1	0	0	0	0	0	0
ڻ	1	6.0	6.5	0.75	0.75	27.0	0.5	5.0	0.5	0.5	0.5	0.5
ئ.	-	_	0.81317	1	-	1	1	-	_	-	1	-
V, (eV)	-30,19634	-111.25473	-29.68411	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	9,50874	23.87467	8.04432	38.92728	25.78002	12.87680	9,33352	9,33352	9.37273	9.33352	9.37273	9.37273
T (eV)	7.37432	42.82081	6.38036	- 32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (vV)	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3,45250	-3.45250
E(m in) (eV)	-14,63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
At How (un m) (aV)	0	-2.69893	-1.44915	. 0	0	0	0	0	0	0	0	0
$E_r(\omega m)$ (cV)	-14,63489	2,69893	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$E_{\rm r}(u_i, \omega)$ (eV)	-31.63534	-63.27074	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	-31,63535
$E_r(atom - atom, mxp^3, AO)$ (eV)	-1,44915	-2.69893	-1.44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
$E_r(so)(cV)$	-33,08452	99696:59-	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
a (1013 rad / s)	16.4962	59.4034	7,42995	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E_{κ} (eV)	10.85807	39.10034	4.89052	16.40846	15.97831	15,91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$ec{E}_n$ (eV)	-0.11568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Eins (cV)	0.14655 [28]	0.21077 [12]	0.09063	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312 f2]	0.12312
Exp (aV)	-0.14240	-0.30266	-0.09943	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
F. em. (cV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0,14803	0.14803	0.14803	0.14803
Erberry (cV).	-33,22692	-66.57498	-33,18395	-67.92207	49.80996	-31.70737	-33.59732	-33.49573	-33.24376	-33.59732	-33.18712	-33.18712
Emma le, w m) (eV)	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
Estate (c. 10 m) (cV)	0	۵	0	-13.59844	-13.59844	-13.59844	0	0	O	0	0	0
12, (rimm) (eV)	3.95714	7.80660	3.76614	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table (5.133. The total bond energies of alky) carboxylic acid chlorides calculated using the functional group composition and the energies of Table (5.102 compared to the experimental values (3).

Formula Name C - C(0) C = C (c) C - C (e) C - C (e) C - C (e) C - C (f) C - C (c) C - C (e) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C - C (f) C:H.CIO

	_													Υ		_
Ехр. <i>в</i>	S			111.6 (acetyl chloride)	121.2 (acety) chloride)	(auedoud) 601	112 (propare) 113.8 (butane) 110.8 (isobutane)	111.0 (butane) 111.4 (isobutane)	108.6 (acatyl chloride) 108.5 (acetone)			. 110.8 (isobutane)		111.4 (isobatane)	111.4 (isobutane)	
Cal. 0	<u> </u>		125.70	110,98	122.13	108.44	110,49	110.49	109.30	109.44	109.44	110.67	110.76	111.27	111.27	107 50
9,																
6	<u> </u>		_								_					L
Φ,	© 						69.51	69.51		70.56	70,56					7,50
E	<u>(</u>		-1.65376	-0.92918	-0.92918	0			c			-1.85836		0	-1.85836	
75"			0.83472	0.86359	0.84522	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
			. –	-	_	0.75	;		0.75			1	0.75	57.0	27.0	
ن			-	0.81317 (Eq. (15.11))	0.81317 (Eq. (15.111)	-			-			_	-	-	-	
<u>ن</u>			-	-	1	1			-			-	27.0	0.75	67.0	
. ی	Atom 2		0,85395 (Eq. (15,113))	0.86359	0,87495				~			0.81549	12210	0.91771	12210	
٠٠,	Alega [0.81540	0.86359	0.81549	0.86359			0,86359			0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization	Designation	(Table 15.3.A)	0	כו	\$	Н			н			25	-	-	1	
E'contraste	Z may		-13,61806	-12,96764 (7)	15,55033	. н			π			-16.68412 C _c	-14.12575 C,	-14.82575 C,	-14.82575 C,	
Atom i Hybridization	Designation	(Table 15.3.A)	72	,	52	7			,			u	\$	w	₽ 1	
F. contratte	Vicini I		-16.68411	-15.75493 C. _A	-16.68412 ()	-15.75493			-15.75493			-16 68412 (',	.7) LEGSS:21-	ردوج: دا. رئ	-15.55033 C ₄	
2c' Teminal	_		4.5826	5.1539	4,9841	3,4252			3,4252			4.7958	££91.6	4.1633	4.7958	
2¢.			2.37954	3,38271	1,38271	211106			2,0971			2.91547	2,11323	1.09711	1.90317	
2c°	(a,)		2.86175	2.86175	1.27954	2.11106			2.09711			2.91547	2.91547	2.91547	1,90327	
Assemb of Asygle			\(\alpha'.\ta'\)	70.5.77	ZOX:,C1	Methybra ZHC, H	כניניני.	ZC,C,H	Н". JH7 7HC." Н	ZC,C,C;	ZC,C,H	حدرد در نه در	רנ"נ" <i>H</i> אנ"נ"	H, 7, 72	حديدير. احد د.	7C,C,C,

CARBOXYLIC ACID ANHYDRIDES ($C_n H_{2n-2} O_3$, $n = 2,3,4,5...\infty$)

The alkyl carboxylic acid anhydrides, $C_n H_{2n-2} O_3$, have two (O)C - O moieties that each comprise C = O and C - O functional groups. The single bond of carbon to the carbonyl carbon atom, C - C(O), is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C - C bonds can be identified. The n-alkane C - C bond is the same as that of straight-chain alkanes. In addition, the C - C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C - C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride C = O and C - C(O) groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of $E_{\tau}(atom-atom,msp^3.AO)$ given in these sections are -2.69893~eV and -1.44915~eV, respectively. The C-O group is also equivalent to that given in the Carboxylic Acid Esters section except that $E_{\tau}(atom-atom,msp^3.AO)$ is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the C-O group, $E_{\tau}(atom-atom,msp^3.AO)$ is $-1.65376\,eV$. It is based on the energy match between the O AO and the $C2sp^3$ HO of each C-C(O) group and is given by the linear combination of $-0.72457\,eV$ (Eq. (14.151)) and $-0.92918\,eV$ (Eq. (14.513)), respectively. This matches $-0.72457\,eV$, the energy contribution of each of the $C2sp^3$ HOs to each C-C(O) functional group, with that of the corresponding energy component of the C-O group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each $E_{\rm D}(G_{\rm roup})$ of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 15.135. The symbols of functional groups of alkyl carboxylic acid anhydrides.	ups of alkyl carboxylic acid antydrides.
Functional Oroup	Group Symbol
(0)	(2-0)
C=O (alkyl carboxylic acid anhydride)	0=0
0-5(0)	0-0
CH ₃ group	$C = H\left(CH_3\right)$
CH; group	$C - H \left(C \cdot H_2 \right)$
CH (alkyf) group	#1.)
CC bond (n-C)	(0).))
CC bond (iso-C)	(2)
CC bond (tert-C)	()-()
CC (iso to iso-C)	(a)
(101-5)	(9)
10 40: 24 50 00	

Table 15,136.	The geometrical bo		kyl carboxylic scid anhydri	okyl carboxylic scid anhydrides and experimental values [1]	inental values [1].							
Piraneter	Parameter C – C(O) C = O Group Group		. C-O Group	C - H (CH,) Group	('-H (CH ₂)	C - H Oroup	ر (a) Group	Group	C~C (e) Group	C-C (d) Group	C-C (e)	Group Group
σ (a _n)	2.04740	1,29907	1.73490	1.64920		1.67465	2.12499	2.12499	2.10725	2.12499	2,10725	2.10725
c. (o _n)	1.43087	1.13977	1.31716	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1,45744	1.45164	1,45164
Bond Lenyth 2c' (A)	1.5143.7	1,20628	1,39402	1,10974	1,11713	1,11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond	1.520	110	1,393	1 107		(1.532	1.532	1.532	1.532	1.532	1.532
£ 3	(accome)	(acetic acid)	ė	(C = 17 propane)	(C - H propane)	(isobatane)	(propare)	(propane)	(propane) 1.531	(propane) 1.531	(propare) 1.531	(propane) 1.531
	(2-butanone)		,	(C - H butme)	(C-H butane)		(butanc)	(butanc)	(butane)	(butane)	(butane)	(butane)
h,c (a,)	1,46439	0.62531	1.12915	1,27295	1,29569	1,29924	1,54616	1.54616	1,52750	1.54616	1.52750	1.52750
2	0.69887	0.87737	0.75921	0.65580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. R.R. R. are H or alkyl groups.	refricti bon	o parameters or	alkyl carooxylic	acid amiyanines	י עיע ע שעב	on any had		the state of the state of the	· · · · · · ·						
Bond	Atom	E,	E,	E,	£,	Final Total	To the same of	Ź	Frantan	$E(C2sp^2)$.0	. '0	9,	ď	ď,
		(cV) Bond I	(eV) Band 2	(eV) Bond 3	(eV) Bond 4	Chy, (eV)	(g)	(a)	Final	(eV)	©	©	©	(%)	(%)
RC,H,C,(O)-O,-C,(O)C,H,R	0,	-0,82608	-0.826££	۰			1,0000	0.82562	-16 47951		27.56	81.8	46,34	1.19766	0.11949
RC, H, C, (0) - 0, - C, (0) C, H, R	٠٠	RKSZX.Q-	-1.34946	-0.826RB	Б	-154.51660	17716.0	0.76753	17,72667	-17,53580	93.21	86.79	47.74	127417	0.0NZ93
RC,H, (R'C,H,C,(O,)O)C, = O,	o	34946.1-	۰	a	D		1,00000	211140.0	.16.17521		12,781	42.73	16,31	0.52193	0,61784
RC, H; (R'C, H; C, (O,)O) C, = O,	٠,٠	. 1 3wydf	-1,72457	-0.NZGKR		.154.51660	17116.0	0.76753	-17.72667	-17,53580	134.08	45.92	97.59	0.60583	0.53394
RH,C, -C,(0)OC,(0)C,H,R	٠	-0.72457	-1,34946	-0,42548	e ·	154.51600	17716.0	0,76753	17,72667	-17,53840	58.55	121.45	26.56	1,83133	0.40045
H,C, - C, (O)OC, (O)C,H,R'	ď	-0.72457	۰	С	0	.152,34026	17719.0	0.87495	-15.55033	15.35946	נשינע	86.301	34.98	1,67762	0,34675
$RH_2C_s - C_s(0)OC_s(0)C_sH_1R^s$ $R = aR_3d$	7.)	-0.72457	-4.92918	u	0	-153,20945	17716.0	0.82562	18647931	-16.28865	07'19	112.60	31.36	1.74821	45,715.0
С-н (сн.)	ر.	810Z6'0-	0	٥	5	.132.544X7	- 17716.0	0.86359	15.75493	15.56407	07'1	12.001	41,48	1,23564	0,18708
C-H (CH,)	ر.	-0.92918	-0.9291Я	a	G	153,47406	161171	0.81549	16.68412	-16,49325	£4.89	111.53	35.84	135486	0.29933
C-H (CH) (ii)	ů.	.0,92918	-0.92918	-0.92918	5	PEEDY'951-	0.91771	14277.0	-17,61330	-17,42244	61.10	18.70	137	1.4238	0,37326
(נ. – נ. (a)) H'נ"נ'H'נ.h' –	Ü	-0.92918	ď	С	٥	.152.54487	0,91771	0.16359	.(5.73493	13,56407	63.13	116.18	30 0%	67868.1	90.38.106
H,C,C,H,C'H, -	5)	81626'0-	.0,9207K	в	-0	-(53,47406	122100	0.81549	-16,68412	-16,49325	14:95	123.59	36.06	1.90890	0.45117
$R - H_1C_1C_1(H_2C_1 - R)HCH_2 - (C - C_1(b))$	55	81626'0-	-0.92918	R1020.0-	0	-154,40324	177160	74,477.0	-17,61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
(C-C,C)	ئ •	#1626.0-	-0,72457	-0.72457	-0.72457	-154.71860	0.91771	0,75889	-17.92866	67.55.71.	48.21	131.79	21.74	LET24.	0.50570
$kaC_{s}C_{s}(H_{s}C_{s}-R)HCH_{s}-(C-C,C)$	ڻ	-0.92918	+0.9291#	-0,92918	0	+154,40324	12216'0	74 <u>477</u> ,0	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
((V-C, (0)))	2)	-0,72457	15t210-	-0.72457	-41.72457	-154,31399	ונגוהט	0.76765	-17.92866	-(17.7379	30.04	%दा	22.66	1.94462	0.49298
(C-C, (f))	τ.	-0,72457	#1020;0-	\$1626'tr	. 0	-154.19863	11116.0	0,78155	69307'21-	-17.21783	11.75	27.73	8.04	1.92443	0.47279
$i \cot_{x} (W - H_{2}C_{x})C_{x}(W^{*} - H_{2}C_{x})CH_{x} - G_{x}C_{x}$	5.5	-0.72457	45457 0-	-0.72457	41.72457	-154.51309	17710.0	89292'0	99826'21-	-17.7779	≯0°05	129.96	9972	1.94462	0,49298

r 15 137. The MO to HO intercent means that have masters of alkel cachoovlic acid anhydrides. R. R. R. are H or alkel errums. E. is E. ∫atom = atom mash AC

Table 15, 138. The energy parameters (eV) of functional proups of alkyl carboxylic acid nahydrides.	ers (eV) of function	nal proups of alky	carboxylic acid a	subydrides.								
Parameters	(O) - (C) (O) (O) (O) (O) (O) (O) (O) (O) (O) (O	0 = 0 0 ± 0	O-O	(.H,	; ;	Craup Graup	Group	C-C (9)	(3) U=U	(g) 0-0	(C) ggg	€ diago
	-		-	Cironia	C. C.	-		-		-	-	-
	-	,		,	•	-						
".	0	0	0	2	-	0	٥	٥	0	٥	c	0
n,	0	0	0	0	0	0	0	0	0	0	0	- 0
,	0.5	0.5	0.5	0.75	0.75	6.75	0.5	0.5	6,0	6.5	5.0	0.5
	-		1	1	1	1	-	-	1	1	1	1
	-	_	-	-	-	1	-	-	-	-	-	-
رڌ	17716.0	0.85395	0.85395	17716.0	12216.0	1/416'0	0,91771	0.91771	177160	17716.0	12216'0	17716.0
	0	2	c	o	1	1	o	o	o	-	1	0
٠,٠	2	4	2	-	1	1	7	7	2	2	2	2
	0	0	0	3.	7	ı	0	0	0	0	0	0
, ±	-	6.5	0.5	0.75	0.75	6.75	0.5	6.5	6.5	\$"0	\$0	0.5
. A	1	-	-	1	1	1	-	1	1	1	1	
V, (eV)	-30.19634	-111,25473	-35.08488	107.32728	-70.41425	-35.12015	-28.79214	-28.79214	29.101.12	-28.79214	-29.10112	-29.10112
V, (aV)	9.50874	23.87467	10,32968	38,92728	25.78002	12.87680	9.33352	9.33352	9.37273	23555.6	9.37273	9.37275
T (aV)	7.37432	42.82081	10,11150	32.53914	21.06675	10.48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
V. (aV)	-3.68716	-21.41040	-5.03575	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(.n no) (eV.)	-14.63489	0	-14,63489	-13,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	15.56407	-15.35946	-15.35946
DE "1, se (se m) (eV)	0	-2.69893	-2.69893	O	0	0	0	0	0	0	0	0
1; [to no) (eV)	-14.63489	2.69893	-11.93596	-15,56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-13,56407	-15,35946	-15.35946
E. (n, w) (cV)	-31.63534	-63.27074	-31,63541	-67.69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31.63535
$E_T \{atom - atom, msp^2, AO\} (eV)$	-1.44915	-2.69893	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E, two (cV)	-33.08452	-65.96966	23.28912	-67,69450	-49.66493	-31.63537	-33,49373	-33,49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 ¹³ rαd /.r)	16.4962	59,4034	24,3637	24.9286	1572.42	24.1759	9.43699	9,43699	15,4846	9,43699	9.55643	9,55643
Ex (eV)	10.85807	59.10034	16.03660	16.40846	15.97831	15.91299	621129	6.21159	10.19220	6.21159	6.29021	6.29021
E, (eV)	-0.21568	-0.40804	-0.26373	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	96802.0-	-0.16315	-0.16416	-0.16416
E (cV)	0.14655	0.21077 [21]	0,13638	0,35532 (Eq. (13,458))	0,35532 (Eq. (13.458))	0.35552 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12512 [2]	0.12312	0.12312 f2l
E., (cV)	-0.14240	-0.30266	0.19554	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0,10359	-0.10260	-0.10260
E (aV)	0.14803	0.11441	0,14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803
Ey formy (oV)	-33.22692	-66.57498	-33,48466	-67.92207	96608'6≯	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Eynn (e, 10 no) (cV)	-14.63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emula, wo my (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	c
E. (12-4) (cV)	3.95714	7.80660	4.21488	12.49186	91058,7	10925.5	4.32754	4.29921	3,97398	18641.4	3.62128	3.91734

Table 15.139. The total band energies of alkyl earboxylic soid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values 13].

Formula Name C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(0) = C - C(

Americal Angle 2c' 2c' 2c' C' Administratory Selection of the Calculation emps Ecodory Hybridizion Economic Atom Atom Economic Color	Conserve Hyperdication Comment Local Land	Atom 1 1 Atom 2 Hybridization 1 1 Atom 2 Hybridization 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	// Atom 2	Atom 2 Atom 2 Hybridizaliza	~ —	C ₂	the parameter	s from the p	receding an	gle were us	ed. E., is E	, (atom – atom, m F	(07,11,	-	г	5	c L	
(a _n) Anny (a _p) Anny Designation Ann 2	Anus J Designation Aven 2	Designation Aven 2	Aven 2		Hybridiza Designat	<u>ē</u> . <u>ē</u>	- I	Vien 2	;	,	<i>-</i>	ď,	† (§	ø, ©	ø- ©	e, ©	E. C.	
-16,17521 (Table 15,3.A) .16,47951	-16.17521 (Table 15.3.A) -16.47951	(Table 15.3.A)	15.47051	4	E)	(Table 15.3.A)								 	=		 ;	-
2.65431 4.3012 0, 12	() (2	21		ė		72	0,84115	0,82562	-	-	-	0.K3339	-1,44915			 	00.221	(21.7 (36)
×	7. 3%	×		C.		×	0.78617	0,71617	-	-	-	0.74617	-1.85836			-	1709	115.8 (36)
2.86173 2.63431 4.4944 -15.55033 5 -13.61206	-15.55033 5	•		-13,61806	ĺ	٥	0,87495	0.85395	-	-	-	0.86443	31077		1	+		(sectic unhydride)
2,46173 227954 4,6362 -16,47951 21 -13,61806	-16.47931 21	ız		-13.618D6		۰	0.82562	0.R5395	_	-	-	0.626.0		I	1	+	ca.vo	(sectic animaride)
2,11106 2,1110h 3,4252 -15,75403 7 H	-15.75493 7	7		=	l	Ŧ	0.86359	-	-	-	0.75	1,15796	0		+	1	7. de	101
															1,	 		(propane)
					- 1									e ga			10.49	(butanc)
										•				15.69		-	61.01	(butane)
209711 209711 3.4252 -11.75493 7 H	-13.75493 7		7 H	r	i	Ξ	0.86359	_	-	-	6.75	1.15796	٥			+-	5	(fsobstanc) 108.6 (ncay) chloride)
				-	- [1	_	_	(acctone)
				+			-					1		70.56	1	-	109.44	
2,91347 2,91547 4,7958 -16,68412 23 -16,68412	-16.64412 23	R		-16,62412		×	0.5150					1		8,01	+	+	147.001	
	15.15033		-1412575	-1412575	- 1			ĵ.	-	-	-	0.81549	-1.85R36			=	110.67	110.R (recleutane)
5	ر" ۽	5	٤ (۲	ن		_	0.87495	0.91771	57.0	_	0.75	1,04887	•	_		=	110.76	
2.01547 2.07711 4.1633 -15.53033 5 -14.12573	-15.55033	,	s -14,13575	-14.8355 C.	l	-	0,47493	1771670	67.9	-	0.73	1,04887	0		-	+	11.11	11.4
2,00327 2,00327 4,793K -11,55033 5 -14,82573	-15,55033 5	_	3 -14,82373	-14,82375	1	-	0,R7495	17710.0	8	-	5	1	, end	╁	+	+	+	(sobutene)
			;	;							;) I	-1.636.30			=	11.27	(usphutane)

NITRILES $(C_n H_{2n-1} N, n = 2,3,4,5...\infty)$

The nitriles, $C_n H_{2n-1} N$, comprise a $C \equiv N$ functional group, and the single bond of carbon to the nitrile carbon atom, C - CN, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and 5 may comprise methylene (CH_2) , and methylpne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C - C bonds can be identified. The n-alkane C - C bond is the same as that of straight-chain alkanes. In addition, the C - C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C - C bonds comprise functional groups. The branched-chainalkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile $C \equiv N$ is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for $\Delta E_{H_2MO}(AOIHO)$ is two times that given in Eq. (14.343), 16.20002 eV, in order to match the N AOs to that of the nitrile $C2sp^3$ HO having a bond order 15 of three. $E_T(atom-atom,msp^3.AO)$ of the $C \equiv N$ functional group is $-1.56513 \, eV$ (Eq. (14.342)) corresponding to the third-order bonded $C2sp^3$ HO.

The C-CN functional group is equivalent to that of an alkyl C-C group given in the Continuous-Chain Alkanes section except that $E_T(H,MO)$ and \overline{E}_{KWb} are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section, $E_T(atom-atom,msp^3.AO)$ of the 20 alkyl C-C group is -1.85836~eV where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded $C2sp^3$ HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each $E_D(Gimp)$ of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mog} that is subtracted from the weighted sum of the

 $E_D(G_{MNMP})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the $C \equiv N$ group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbol.	Table 15.141. The symbols of functional groups of nitriles.
Functional Group	Group Symbol
CCC	() ()-0
20	Z III
CH, group	C - H (CH,)
CH1 group	C-H (CH,)
CH (alkyl) group	
CC bond (n-C)	(E) (J-)
CC bond (iso-C)	(0)
CC bond (ten-C)	(9)
CC (iso to iso-C)	(g) U= 0
CC (1 to t-C)	(e) ()=()
CC (t to iso.C)	G-0-0

() 2~2	dies .	20001	77,017	1.45164		1.53635		1532	(propane)	1,531	(butane)		05/75	
(a) 3-3	Croup	2001 6	2101-2	1.45164		1,53635		1.532	(propane)	1.531	(butanc)	02613.1	06/26.1	000070
(P) 2~2	dnoin	2.12499		1.45/44		1.54280		1,532	(propane)	1.531	(butane)	7 57515	1:5010	009890
C-C (c) Groun	, and	2.10725	7 46.16.1	1.43.04		1,53635		1.532	(propane)	1.531	omane)	05165		0 68888
C-C(b)		2.12499	1 45744	A STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STA		1.54280		1.532	(propane)	15.7	(millante)	1.54616		0.68600
C-C(a) Group		2.12499	1 45744			1.54280		1.532	(propane)	1331	Tonigille	1.54616	00000	0.08900
C - H Group	ļ	1.67465	1.05661			1.11827			(irohutana)	(DIEDOCO)		1.29924	20000	0.02073
C-H(CH ₁)	dioin	1.67122	1.05553		,,,,,	2011	2.) (- 1/2 prompts)	1117	(C-H butane)		69567	03/1290	2.00.0
C-H (CH,)	, , ,	1.04920	1.04856		1 1007.4	*****	100	(C - H armane)	1.117	(C - H butane)	2000	1.27233	0.63580	
Crav Group	ישטער ז	עקנאביי)	1.09813		1,5521			1.159	(acetonitrile)		0,404.0	0707470	99100	
(i) Croup	1 91755	200	1.38295		1.46365			1.468	(acctonitrile)		1 382110	21170	0.72309	
rarameter	0 (0.)		c' (a,)	Bond	Length High	3c. (A)	Fra Bond	Length	5		h.c (a.)		a	

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Table 15.145. The MO to HO intercept geometrical bond parameters of nitril	erreal bon	d parameters of	nimies. K,R,A	ies. K, II, K are II of alkyi groups. Ey is Er (ainii – ainii, iiky AU)	ri Broughs. 2, 13	$c_r(a_{lom}-a_{lc})$									
Bond	Atom	£,	5,	E,	Ę	Final Total]	آء	Ecuipm	$E(C2sp^2)$	ie.	6	6	ď	ď
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy ('24p	(*)	(%)	(eV) Final	(eV)	E	©	C	(°)	(a)
RH.C.C = N	2	-0.78257	۰		۰	3	0.93084	0.87170	-(5.60132		17701	32.99	72.74	0.36690	0.73114
RH.C.C. = N	ز	-0.78257	-0.92918			-153,32744	0.91771	0.82272	-16.53750	-16.34664	155.42	34.58	35.50	0.42077	0.67736
RHiC, -C,N	ن	40,92918	-0.18257			-133,32744	17710.0	0.82272	-16.53750	-16.34664	81.32	89'86	38.00	1.50718	0,12423
H,C, - C,N	ij	-0.92918		۰	۰	-152.54487	17716.0	0.86359	-15.75493	-15.56407	85.50	24.50	40.67	1.45066	17790.0
RH,C,H,C, -C,N R=alkyl	ڻ	81626.0-	-0.92918	С	0	-153,47406	17716.0	0×518.0	-16.68412	. 16.49325	80.83	74,00	37.51	1,51718	0.13423
C-H (CH,)	ر.	-419291X		c	٥	-152.54487	14216.0	686389	-15,75493	-15.56407	77.49	102.51	41.48	1,23564	0,18708
C-H (CH;)	ti	40,92918	-0.9221H	6	۰	-153.47406	17710.0	67518'0	-16,68412	. 16.49325	68.47	11.53	35.84	1.35486	0.29933
C-H (CH) (ii)	ti	-0.92918	-0.92918	41626.D-	•	-154,40324	17719,0	0,77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
H,C,C,H,CH,~ (C - <u>C</u> (a))	' '	41,9291K	6	G	0	-152.54487	17710	0.86359	-15.75493	-13.56407	63.82	116.18	30.08	1.83879	0.38106
('U-C'('N'CH''-	ر.	#16ZG15	#1620.02	¢	o	-153,47406	17716.0	0.81549	-16.64412	.16.49325	19.08	123.59	26.06	1.90190	0.45117
$n-H_1C_2(H_1C_4-R)HCH_1-$ (C-C (b))	ڻ	आव्यत:0-	81/02/0.0-	0.92918	c	-154,40324	17714,0	0,77247	-17.61330	.17,42344	0.14	131.70	21.50	1.97162	0.51388
$R - H_1C_*(R' - H_1C_*)C_*(R'' - H_1C_*)CH_1 - (C - C'(c))$	55	4.92018	-0.72457	-0.72457	-0.72457	-154.71860	0,91771	0.75119	-17,92806	917.71.	12:87	131.79	21.74	1,95734	0.50570
(G - G (d))	٠ ر٠	H1020:0-	-0.9291A	-0,92918	o	-154,40324	וענים	0.77247	-17,61330	-17,42244	05,30	131.70	21.50	1,97162	0.51388
(C-C(0))	5	TSMCT.0-	-0.72457	-0.72457	-0.72457	-134.51399	17710,0	0.76765	-17.92866	917.73779	50.04	129.96	22.66	1.94462	0.49298
$lenC_{\mathcal{C}_{\bullet}}(H,C_{\bullet}-R)HCH_{\bullet} (C,-C,(9))$	55 -	-0.72457	н годо: 0-	0.92918	.0	-134,19863	17716.0	\$\$184.0	-17,40169	-17.21783	82.28	22.121	24.04	1.92443	0,47279
$hoC_{*}(R'-H_{*}C_{*})C_{*}(R'-H_{*}C_{*})CH_{*}-$ $(C-C_{*}(f))$	ů	72,57.0-	-0.72457	.0,72457	451-27.0-	-154,51399	0.91771	0.76765	-17.928GA	-17.73779	50.04	129.96	22.66	1,94462	0.49258

Parameters C - C (i) C as N Group Group	C-C (i)	Cre A		*.	H-)	(¥) ::-';	(c-c (p)	(c) C-C	C – C (d)	(; - (; (e)	(J-C (I)
2	. -	,	Crotto	Group	dnoin	dnoun	Croup	Group	Group	Graup	Group
	-	,		,		-	-	1	_	-	-
"13	5	О	2	-	0	0	0	0	0	0	c
n;	0	٥	0	0	0	0	0	0	0		
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	50	١	3
<u>.</u>	1		-	_	_	-	-	-	-	3 -	g .
<i>c,</i>	-	-	-	-	 - _	-	-	. -	- -	- -	-
63	17716.0	0.91140	0.91771	0.91771	177100	0.91771	166190		- 3	-	-
ر دا	o	-	0	-	-	0		0.91771	17/16/0	0.91771	0.91771
ر.	2	°	-	-	_	, ,	, ,	,	_	-	0
ั้ง	0	c	-	,			7	7	7	2	2
	>0	, ,	, ,			0	В	0	٥	0	0
	3 -	g.	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	5.0
7 (40)	-	-	-	-	-	1	-	-		_	-
(42)	-33.01231	-207.49229	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
(ja) 4.	9.83824	37.16984	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9.37273	1177719
(49) /	8.63043	86.03250	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6 905001	6 00500
(67)	-4.31522	-43.01625	-16.26957	-10.53337	-5.24291	-3.38732	-3,38732	-3.45250	-3 38737	3.45350	0.50500
E (20.10) (CV)	-14.63489	32,40004	-15,56407	-15.56407	-14,63489	-15.56407	-15.56407	9763851-	15 56007	3,436046	-3.43230
William (aV)	-1.85837	0	0		0	0	•		200	0+605.01.	-15.35940
12 (no no) (aV)	-12.77652	32,40004	-15.56407	-15 56407	0875771	16 56 507	, , ,	,	>	0	0
E, (4,20) (eV)	-31.63537	94 90616	12497 73-	40 66403	10000011	10.00401	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
E (drom = glom assa) AO) (V.)	76836	2000	10,00	-47.00473	-31.03533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
E (m) (cv)	00000.1	-1.30313	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
(10)	47.650.66	-90.4/124	-07.09450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
to (in realis)	19,2516	22.0753	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
7. (ev)	2.67172	14.53031	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	621159	6.29021	6.29021
()) (()	-0.23388	-0.24250	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0 16416	16416
G(1) (CV)	(37)	0,28107 [37]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Fo (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
E, (cV)	-0.17884	-0.10197	-0.22757	-0.14502	-0.07200	-0 10340	14 O	15031.0	[2]	[2]	[2]
E (cV)	0.14803	0.14185	0.14803	0.14803	0.14803	0 14803	0.14903	-0.13924	-0.10339	-0.10260	-0.10260
\mathcal{L}_{γ} (dump) (cV)	-33.67258	-96.77713	7077079	AD ROOM	31 70332		20041.0	0.14003	0.14803	0.14803	0.14803
Essent (s. 10'10) (cV)	-14,63489	-14 63489	PALTA 81.	14 63480	14 62 485	33,39/32	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E.m. (A. 10 m) (aV)	0	-	-13 50844	12 50044	11.03409	-14.03489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E, (cm.) (dV)	4.40280	8 87594	12 40194	7 07016	-13.39844	0	0	°	0	0	0
	2070	0.04234	12,49160	4.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3,62128	3.91734

72.50

Table 15.145. The total bond energies of nitriles calculated using the functional group composition and the energies of Table 15.144 composed to the experimental values (3). The magnetic energy E_{***}, that is subtracted from the weighted sum of the E_o(coo) (eV)

			Granp Granp	Z ≡ Z Group	E	CH,	H.)	C = C (a)	ر-ز (p)	(c) C-C (c)	0-0	C-C(q) . C-C(e)	ľ	(J-C (I)	E	Colculated		- 1	Relative Error
N'H'O	Acetonitrile				-	c	0	5	c			ľ			,	Total Bond Factory (eV)	Total Bond Energy (aV)		
	Butmentirile					r	.		6		0 0	0			۰.	25.72060			PC100'0
	-Methylpropanenity	ŧ	-	-	. ~	۵.•	s	7 5	c •	0 (c	c				50.03600			0.00171
	Z-Dimenvince	441		_	_		c	. m	7 C	c c	c (C 1		c	c	50,13689			0000
	spinenink				- , -	۵.	0	2		• •	- 0	9 6		0 4	٥,	62.19370			1100
	Cumentific		_	-		r. ve		'n	c	0	c	c		• •		787779			0.00132
	Decomeninie Terradeconenitriie					: ≠ :	0	s æ :	o;0		۰ د	٥ ٥				98.66680			0.00069
						71	a	7	٥	c	0	١٩				122,98220			0.00057
e 15.146.	5 Table 15.146. The bond angle parameters of nitriles and experimental values [1]	parameters of	f nitriles and	experimental		e calculation o	In the calculation of $ heta$, the parameters from the precedim angle was used	3 from the ores	median saule		, ,		19					1	
Atoms of Angle		_	75.	5	Atom	.,,	Ainm 2		2.9		a Cr ann	Cr ts Cr (dittill - didin, m.th .AO)	.40).						
	(6,	(a)	Norse (Og)	-	Hybridization Designation	Contrade: Aloun 3	Hybridization Designation	April C	V Von 7	ن- 	ۍ.	<u>"</u>	٧٠,	E, E	0, 3	o 3	9,3	Cal. θ E	Exp. 6
W.J.J/			+		(Toble 15.3.A)	-	(Table 15.3.A)								<u> </u>	 E	_		2
	†	-	┥								ĺ				1		1	-	-
H, 147	2,09711	1 209711	3.4252	-15.75493	,	=	Ξ	0.86350	-	1	1							OX.	
ZHC.C.									-	1	-	0.75	1.157%	٥		_	5	109.50	
Making /	21106	2 1106	3.75												70.36		<u> </u>	109,44	109.7 Geografields
	T	十	+	20000		ı	Ξ	11.86359	-	-	-	0.75	1.15796	c			Ĩ.	TT YOU	107
J',J',J',J7	<u>.</u>										 -							. E	112 ropane)
															15.03		<u>=</u>	10.49	Putane.
H J J/											\dagger					1		(3)	buttene)
11.00											•				69.51			4)	e (1)
Melty H	1,007	20211	3,4252	14.25.001								+					: 		Li.4 Suttens)
 70		-			.	E	r	0.Hr.359	-	-	-	0.75	1.15796	0			05.001	<u> </u>	2 201
H, 7, 22															70.56	-	100.44	4	
7C'C'C.	_	├		-16,68412		-16.68412					1				70.56		109.44	3	
ن ز پ	1	ACIES .	4.795K	ڻ	ສ	ť	n	0,815-49	0.RIS-49		-	-	0.81549	-1.85836			110,67	├	110.8
L, C, H	2.91547	211323	4.1633	-15.55033 C.,		-14.X2575 C.	-	0,87495	17710	6,75	-	220	- Sign			-	+		utane)
H.7.37	2.91547	11602	4.1633	-15,35033		-14.H2575	1			-	+	+		-		\dashv	110.76	9	
70.02	2 90177	7,000	a Just	-15.55/133	,	-14,K2573	-	CGP/#11	0.91771	6,75	-	a.75	1.04KK7	0			111.27		(sobutare)
7.C.C.C.				ئ	~	U	-	0,87495	0.91771	0.73		82.0	1.04887	•1.RSkG6			11.127		111.4 Grahman
								_		-	-	+	+			+	+		

THIOLS
$$(C_n H_{2n+2} S_m, n = 1, 2, 3, 4, 5...\infty)$$

The alkyl thiols, $C_n H_{2n+2} S_m$, comprise a SH functional group and a C-S functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the SH functional group is solved using Eq. (15.41). As in the case of the C-H bonds of CH_n n=1,2,3, the S-H-bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the S3p shell. The energy of the H_2 -type ellipsoidal MO is matched to that of the S3p shell and comprises 75% of a H_2 -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of S, E(S)=-10.36001~eV, is less that that of H, the linear combination of the H_2 -type ellipsoidal MO with the S3p shell further comprises an excess 50% charge-density donation from H to the S3p shell of the S-H-bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four 3p electrons. From Eq. (15.12), the sum $E_T(S,3p)$ of the energies of S, S^+ , S^{2+} , and S^{3+} [38] is

$$E_{T}(S,3p) = 10.36001 \ eV + 23.33788 \ eV + 34.79 \ eV + 47.222 \ eV$$

$$= 115.70989 \ eV$$
(15.118)

By considering that the central field decreases by an integer for each successive electron of the shell, the radius r_{3p} of the S3p shell may be calculated from the Coulombic energy using Eqs. 25 (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)} = 1.17585a_0 \tag{15.119}$$

where Z=16 for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy $E_{Coulomb}(S,3p)$ of the outer electron of the S3p shell is

$$E_{Condomb}(S,3p) = \frac{-e^2}{8\pi\varepsilon_0 r_{3p}} = \frac{-e^2}{8\pi\varepsilon_0 1.17585a_0} = -11.57099 \ eV$$
 (15.120)

The sharing of the electrons between the S and H atoms permits the formation an S-H-bond MO that is lowered more in energy than the participating S3p orbital which consequently increases in energy. By considering the 50% electron redistribution in the S-H group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius r_{S-H3p} of the S3p shell may be calculated from the Coulombic energy using Eq. (15.18)

$$r_{S-H3p} = \left(\sum_{n=12}^{15} (Z-n) + 0.25\right) \frac{e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)}$$

$$= \frac{10.5e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)}$$

$$= 1.23465a_0$$
(15.121)

where the s=-1 in Eq. (15.18) due to the charge donation from H to S. Using Eqs. (15.19) 10 and (15.121), the Coulombic energy $E_{Coulomb}(S_{S-H},3p)$ of the outer electron of the S3p shell is

$$E_{Coulomb}(S_{S-H}, 3p) = \frac{-e^2}{8\pi\epsilon_0 r_{S-H3p}}$$

$$= \frac{-e^2}{8\pi\epsilon_0 1.23465 a_0}$$

$$= -11.01999 eV$$
(15.122)

Thus, $E_r(S-H,3p)$, the energy change of each S3p shell with the formation of the S-H-bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$E_{T}(S-H,3p) = E(S_{S-H},3p) - E(S,3p)$$

$$= -11.01999 \ eV - (-11.57099 \ eV)$$

$$= 0.55100 \ eV$$
(15.123)

15 Then, in Eq. (15.42):

$$E_{r}(AO/HO) = E(S) - E_{r}(S - H, 3p)$$

$$= -10.36001 \ eV - 0.55100 \ eV$$

$$= -10.91101 \ eV$$
(15.124)

And, in Eq. (15.56),

$$E_r(atom - atom, msp^3.AO) = 0.55100 \text{ eV}$$
 (15.125)

Due to the charge donation from H to S, $c_1 = 1$ in both Eqs. (15.42) and (15.56). As in the case of the C - H-bond MO, $C_1 = 0.75$ based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is also one, and the energy matching condition is determined by the C_2 parameter. Using the energy of S, $E(S) = -10.36001 \, eV$ in Eq. (15.65), the hybridization factor C_2 of Eq. (15.52) for the S - H-bond MO is

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144$$
 (15.126)

Since the energy of S is matched to the Coulombic energy between the electron and proton of H, $E(H(a_0)), \qquad \qquad E_{initial}(c_{\bullet,AO/HO}) = E(H(a_0)) = -13.60580 \ eV,$

- 10 $E_{initiol}(c, AOIHO) = E(H) = -13.59844 \ eV$, and E_{mag} is that corresponding to $E(H(a_0))$ given by Eq. (15.58). $E_D(Group)$ for hydrogen sulfide is equivalent to that of the SH functional group, and the $E_D(Group)$ (eV) for dihydrogen sulfide follows the same derivation as that for the SH functional group except that the parameters correspond to $n_1 = 2$ rather than $n_1 = 1$ in Eqs. (15.42) and (15.56).
- Furthermore, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with E(AOIHO) = 0 and $E_T(AOIHO) = \Delta E_{H_2MO}(AOIHO)$. Then, the solution of the C-S functional group comprises the hybridization of the 2s and 2p AOs of C to form a single $2sp^3$ shell as an 20 energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. Then, $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a 25 corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the S AO has an energy of $E(S) = -10.36001 \, eV$. To meet the equipotential condition of the union of the

C-S H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.51) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO \text{ to S}\right) = \frac{E(S)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965 \quad (15.127)$$

Since the sulfur is energy matched to $E(H(a_0))$ in the S-H-bond MO, $E_T(atom-atom, msp^3.AO)$ of the C-S-bond MO in Eq. (15.52) due to the charge donation from the C and S atoms to the MO is -0.72457~eV corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 10 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted 15 from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the HCSH group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CSH group (no H bonds to C) were each treated as a tert-butyl C-C. E_{mag} was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

Table 15.147. The symbols of	Table 15.147. The symbols of functional groups of alkyl thiols.
Functional Group	Group Symbol
SH group	153
H ₂ S	HS
CS	, n
CH, group	С-н (сн.)
CH, group	C-H (CH.)
£	; a;
CC bond (n-C)	(3)
CC bond (iso-C)	(a)
CC bond (terr-C)	(9)
CC (iso to iso-C)	(E) (J-)
CC (tio t·C)	(G) (J -)
CC (t to iso-C)	() () () () () () () () () ()

			l									
Table 15.148.	The geometrical bo	Table 15.148. The geometrical bond parameters of aikyl thiols	I thiols and experime	and experimental values [1].								
rarameter	$S-H(H_2S)$	HS.	S−2	C-H (CH.)	C-H (CH.)		C-C(a)	(P) (P)	(0)	4,00		
	•	daois	daas	Group	Group	Group	Group	Group	Group	(e) (a)	(e) (c) (c) (d)	€ 0-0
a (a)	1.83762	1.83762	1.90975	1.64920	1.67122	ATAK	2 17400				dnoin	digit
د. (۵)	1 26842	1 268.2	1 31,466				7.15422	4.12459	2.10725	2.12499	2.10725	2.10725
Don't I		71.007	1.71433	1.04856	1.05553	1.03661	1.45744	1.45744	1 45164	1 46944		
	134344								20107-1	P#1641	1.45164	1.45164
70, (7)	#47±01	1.34244	1.81460	1.10974	1.11713	1.11827	1.54280	1.54280	1,53635	1 54280	363631	
Exp. Bond		1.34066	1.819	101	1 103						CCOCC-1	Cadec.
Length	1 3366	(hydrogen sulfide)	(methanethiol)	(C - H monane)	(, L. L. manner)		1.532	1,532	1.532	1.532	1 532	1 532
3	3	75	1.829	1.117	1.117	(Jeophytana)	(propane)	(propane)	(propane)	(propane)	(propane)	(propans)
		(methanethiol)	(ethanethiol)	(C-H butane)	(C-H hurana)	(Manager)	77.	1.531	1.531	1.531	ES.	. 531
b,c (a,)	1,32964	132964	0.84112	30224	1 200.00		(Dutanc)	(butane)	(butane)	(butane)	(butanc)	(butane)
2	1 64075	300000		2	1.43309	1.29924	1.34616	1.54616	1.52750	1.54616	052651	1 63760
		0.07023	0.69778	0.63580	0.63159	0.63095	0.68600	007070	20000		0.000	1.32.130
						-	2000	0.000.0	0.08888	0.68800	U 68888	000000

Table 15, 149. The MO to HO intercept geometrical bond parameters of alkyl thiolis. K, it., if are, H or alkyl groups.	netrical bar	o parameters of	alky more, r.	יי אוני ח	strain finance	T 15 Er (amm	Er is Er anim - onim, usp .Ac. j.	.,							-
Bond	Aforn	£,	£,	Ľ,	Er	Final Total	'}	.3	Ermon	. E(C2.p')	.0	8	9,	d,	d ₁
	<u> </u>	(eV) Bond i	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C2sp ² (C2sp ²)	(°)	(°)	Fing	Final	€	٤	©	(b)	(°)
N-H (hydrogen sulfide) (dihydrogen sulfide)	27:	0.55100	5		e	,	1,32019	1.23465	-11.01999		101.65	71.35	61.62	0.87355	0,39487
RS - H	,	0.36229	0,55100	,	0		1,32010	0.92955	-14.63704		67.09	92.91	44.28	1,31557	0,04714
C. H, -3H	S	-0.36229	0,55100	0	0		01025.1	0.92955	-14,63704		132.06	47.94	55.13	1.09181	0.62274
C,H, -3H	ن	40.36229	0	. 0	0	-151.97798	17716.0	0.89582	-15.18804	-14.99717	69,84	110.16	R8.87	0.03762	1.67072
RC, H,C, H, -C, H,SH	٠	40.36229	40.92918	.o	a	-152,90716	17716,0	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1,18689	0.52765
('-H ('H,)	i,	41.92918	۰	0 .	c	-152.54487	17719.0	0.86359	415.75493	-15.56407	77.49	102.31	41,48	1,23564	0.18708
('-H (CH ₂)	i	\$1626.D	.0.9291#	. 0	e	-153,47406	12216.0	0,81549	-16.68412	16,49325	68.47	11.53	33,84	135486	0.29953
('-H (cH)	į	A192918	-0,92918	81626'0*	đ	-154.40324	17710,0	C14277.0	.17,61330	-(7.42244	61.10	111.90	31.37	1,42588	0.37326
((, -(, (v)) H,C,C,H,CH; -	ن	#1620°U	0	. 0	a	182,54077	17719.0	O.RGUS	-15.75493	-15.56407	23.53	116.18	30.08	1.83879	0.38106
H,C,C,H,CH;	Ú	R1029.D-	61626'0-	0	a	-153.47406	17716.0	0.81549	-16.68412	-16.49325	15.64	9F 121	26.06	1.90899	0.45117
(K-H,C,C,(H,C,-R))HCH,-	Ů.	.0.9291#	#10 2 0,0-	91626'0-	0	-154,40324	12216'9	0.777u	0281970	-17,42244	48,30	131.70	21,90	1.97162	0.51388
$(K-H_2C_a(R^a-H_2C_a)C_a(R^a-H_2C_a)CH_2-(C^a-C^a)CH_2$		-0.9291#	-0,72457	2572275-	-0.73457	-154.71860	17714,0	0,75889	-17.92866	-17.73779	48.21	(31,79	21.74	L.93734	0.505.0
$ImC_{a}C_{a}(H_{a}C_{a}-R^{\prime})HCH_{a}-IC_{a}C_{a}(G)$	ť	-0.9201K	-0,92918	-0.92918	U	-154.40324	17716.0	0.77247	-17.61330	-17,42244	4830	131.70	21.90	20172.1	0.51388
$(u_r \pi', (R'-H_3C_s)C_s(R'-H_3C_s)CH_1 - (C'-C', c))$	ť	-0.72457	-0,72457	1577.0-	12457	15451399	17710.0	0.76763	25826.71.	677.71-	\$0.04	96'621	यह	1.04462	0,49298
$lent(C_{\bullet}C_{\bullet}(H_{\bullet}C_{\bullet}-R))HCH_{\bullet}-(C_{\bullet}-C_{\bullet}(f))$; C*	-0.72457	-0.9291K	-0.92918	0.	-154.19KG3	17410.0	0.78155	-17.40%@	-17.21783	52.78	17.22	24.04	1.92443	0.47279
$ImC_{*}(R-H_{2}C_{*})C_{*}(R^{*}-H_{2}C_{*})CH_{2}-ICC_{*}(R^{*}-R_{2}C_{*})CH_{2}$	5.5	.0,72457	-0.72457	-0.72457	-0.72457	661151511-	122160	0.76763	99826'11-	-17.73779	\$0,04	96'671	22.66	1.94462	0.4929R

Table 15.149. The MO to HO intercept geometrical bond parameters of alky! thiols. R. R. R. are H or alkyl groups. Er is Er (arum ~ annu, msp². M.).

Table	Table 15.150. The energy parameters (eV) of fimetion	lers (eV) of fimetic	yal groups of alky	t thiols.									
Parraim	Parameters	×.	Srowp Gro	ر- ک Group	Spen.	Group	Oroup	Group Group	Crowp Growp	Cuonb Cuonb	Group	C-C (e)	Graup Graup
E		2	-	-	3	2	-	-	-	-	-	-	-
ε.		0	0	0	2	-	0	0	o	0	0	0	0
E		0	0	0	0	0	0	0	0	0	0	0	0
٢		0.75	0.75	0.5	6.75	0.75	0.75	0.5	5.0	0.5	0.5	0.5	0.5
<u> :</u>		0.76144	0.76144	0,64965	_	-	-	1	-	_	1	1	1
J		-	_	-	-	-	-	-	-	1	1	1	1
ۍ ا			-	_	0.91771	17416.0	17716.0	17216.0	17716.0	0.91771	0.91771	0.91771	0.91771
ų.		~	-	0	0	-	-	0	o	0	-	1	0
J.		-	-	2	-	_	-	2	2	2	2	2	2
ت		-	-	0	3	2	-	0	0	0	0	0	D
<u>.</u>		0.75	0.75	0.5	0.75	0.75	0.75	20	0.5	0.5	0.5	5.0	5.0
ال.		0.76144	0.76144	0.64965	-	1	-	-	-	-	-	1	-
7,	(1/2	-72.80662	-36,40331	-46,36495	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	21101.62-	-29.10112
7 (3)	3	21,45310	10.72655	7.93551	38,92728	25.78002	12.87680	9,33352	9.35352	9,37273	9.33322	6.37273	9.37273
7 (97)		19.81003	9.90502	12,13899	32,53914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
7 (3)	eV)	-9.90502	4.95251	-6,06949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E. L.	E(.m no) (cV)	-20.72002	-10,36001	0	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
Δέ",	DE House (w) (aV)	1.10200	0.55100	-0.72457	0	0	0	0	0.	0	0	0	0
12,1.10	E, (.10 no) (cV)	-19.61802	-10.91101	0.72457	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E, la	Er(upin) (cV)	-63.27052	-31,63526	-31.63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(a)$	$E_r(\alpha_{l0m} - \alpha_{l0m}, n_S p^2, AO)$ (eV)	1.10200	0.55100	0.72457	0	.0	0	-1.85836	-1.85836	-1.44915	-1.85836	5164471-	-1.44915
E, (14	Erlind (cV)	-62.16874	-31.08437	-32,35994	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
<u>e</u>	a (10" rails)	12.5415	12.5415	30.5436	24,9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
E. C.	Er (eV).	8.25504	8.25504	20.10434	16.40846	15.97831	15,91299	6.21159	6.21159	10.19220	6:21159	12062'9	6.29021
, C.	(uV)	-0.17669	-0.17669	50182.0-	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	91191'0-	-0.16416
1,500	Liens (cV)	0.32422	0,33620	98146	0.35532 /Eq. (13.458))	0,35532 (Fa (13.458))	0.35532 (Fg (13.458))	0,12312	0.17978	0,09944	0,12312	0.12512	0.12312
12	E. (eV)	-0.01458	-0.00859	-0.24632	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
f.	Eug. (cV)	0,11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E. W.	Er frame) (eV)	-51.10493 ⁸	-31.09296	-32,60626	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
5	(45) (01/01/1)	-13,60580	-13.60580	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-[4.63489	-14,63489	-14.63489
1	E le . 10 111) (eV)	-13.59844	-13.59844	0	-13.59844	-13.59844	-13.59844	0	٥	0	0	0	0
E. (1	Entimy) (ar)	3,78628	3.77430	3,33648	12,49186	7.83016	10925.5	4,32754	4.29921	3.97398	4.17951	3,62128	3,91734
			100000										

 $= E_{r}[a_{-1}a_{1}a] = E_{r}[a_{1}a] - E_{r}[a_{2}] = 62.19789 \text{ eV} - \left(-31.09296 \text{ eV}\right).$

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy E_{ag} that is subtracted from the weighted sum of the $E_{b}(\omega - \omega)$ (eV) values bass Composition is given by (15.58).

	ZEBC		×.	HS.	٦	77.7	1		1				- 1						
			,	e e	֝֞֝֝֝֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓	, ,	֖֓֞֟֝֟֝֟֝֟֝ ֚	5	ت ا ا) - C	(E)	(a) C-C(b) C-C(c) C-C(d)		(e) U-U	(J) (J-)	Ŀ	Catculated	Extrarimental	Refative Frame
3/1			Croup		deals										;	į	Total Bond	Total Bond	
2.5	variation Sulfate		- :	-	٥	e	=	0	-		ľ						Energy (cV)	Energy (eV)	
	בייי הפלכם פתווננ		=	-	c	0	0	٥			•			= :	0	0	1,77430	3653	-0.03320
	We'll tangen ion		-	-		-	0			•	•	. •		0	c	o	7.56058	2,605	0.00582
	ancura o		•		_	-	_	-	: -		= (-	•		19,60264	19.575	0.00141
	- Propancinol		c	-	-	-			- ^		= •				•	E	31,76034	31.762	\$00000
	2 Propancibio		c	-	-	~		:	• •		•	- "		•	0	۰	43.91804	43.933	5,000
2 2 2	Butandhiol		c:	_	-	-	m		-	4 0	0 0	- •		۰.	e	c	44.01893	44.020	0,00003
	John Callo		= 1		-	7	_	-	-			. •			٠.	0	56.07574	\$6.00	0,00024
	The burn of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the bank of the ba		2 1	-	-	~	_	_		• •	•	. •		٠.		0	56 7663	. S6.1X1	00000
	Action 1-2-propaneuron			-	-	_		-		1 <	•	•			•	0	SK 14830	. 56.186	990000
	L-Mathyl-1-butanethiol		-	-	-		~	-		۰ د	- (- 1	. ·	0	0	÷	56,36027	56.313	D DOOK4
•	Culturation		.	_	_	-		. c			•	- '		•	•	0	. 0090EX9	68.314	0.00012
	Child Leading		e :	_	-	m	_	•		•	۰ د	۰,۰			•	•	68,23344	68,264	0.00044
•	2-Dimethy, Locomodus	3	===		- :	۰۰.	c	7	. c	in			-		•	-	6K.51797	(8,44)	-0.00) [3
3	-Hexandhiol		9 5	<u>-</u> .	 .	m	-	٥	-	• =						۰ ۰	68,31552	187.60	0.00095
	britail. 2. non tomothics				_	-	••	0	•	c	, c					7	68.51797	GR.451	-0.000KH
. ,	1. Dimethyl 2 bytanethial				_	-	~	0	~	-	•				٥.	•	\$03911 4	80.416	0,00031
	Hensanchina					7	c	-	•	2	•				۰.	-	10,67367	80,607	-0.00085
SRS	-Decambiol					_	æ	0	·	•	• •		, -	> <	- (-	80.71992	80.603	-0.00143
			2		-		9	0	•	•						0	92.548.84	92.570	0.00023
											1			ь	٥	٥	129,02194	129.048	0.00020
Table 15.152, T.	Table 15.152. The bond angle parameters of alkyl thinks and experimental values [1] In	meters of alk	or ships and	devneriments	al variant [1]	a the material		•				,	٠						
				The second second	al values [1]. II	n ine carculano	ada, nep	arameters from	the caretianon of σ_r , the parameters from the preceding angle were used. E_r is E_r (atom – atom men) $A(r)$	angle were us	sed. E. is E.	atom - atom	T. men' AO						
ard by the summy	Jr.,	, <u>, , , , , , , , , , , , , , , , , , </u>	Zc. /	L	Atom 1	- -	Ahnu 2	-	-										
]	3	Terminet		Hy bridization	Ĭ	Hybridization	٠,	ڻ.	 ز	ს		v	e d	8	٩	A Cal A	Fyn 8	
	- ()			_	1	-		-		_				-	,	-			

					·						_								
	Exp. θ (•)	96.3 (methanshiol)	96,4 (ethanethiol)	(ethanethiol)	107 (propane)	112 (propane) 113.8 (butane)	(sobowe)	(hutsne)	(ixobutane)				1,10,X	(sechulane)		7'11'	(isobutane)	(isobulane)	
	(a)			110.02	108.44	110.49		110.49		109.50	109,44	100.44	10.67		9.9	11.27		7	
	()																		_
	e O	_			_														
	0,0	_	_		_	15.69		(9.51			70.56	70.36		\perp					5
	E _T (aV)	c		-0.72457	o			,		•			-1.H5B36	•		o	92858 I ·		
", msp'. 40).	3	1.(346		0.75257	1.15736					1.157%			0.HI549	1.04887		1,04897	1,04887		_
determine preceding ungle were used. L. 13 L. (aloni - aloni, msp. AO)	u-	0.75		-	0.73					0.75			-	0.75		0.75	6.75		_
s 12.7 13.	ა "	-	20170	(Eq. (15.127)	-	••				-			-	-			-		
THE WILLIAM WE	<u>ل</u>	6.75	•	-	-					-			_	0.75		0.73	0.73		_
ימיי וויים אוברמי	C C	0,86359	0.64965	(Eq (15.127))	-					-			0,81549	0.91771		0.91771	177160		
ב ליוו ווווווווווווווווווווווווווווווווו	√ į	0,76144 (Eq. 13.(23))		1,81349	0.16359			,		O.MAZSIJ			0.R1540	0,87495		0,87495	0,87495		
	Atom 2 Hybridization Dosignation (Toble	S		,	=					z			a	-		-	_		
ł	Promise American	-15.73493	-10,36001	×	=]:			-16.68412	Ç,	-14.82575	-14.82575	ن.	-14.12373	·	
	Atom I Hybridization Designation (Table 15.3.A)	-	*										22	~	.	,	· •		
	Į.į	-10,34001 N	-16,68412	.1	-15.75493				FINDS \$1.			-16.68412	٠:	,13.3303x	-13.55033	J.*	-15,53033		
	Terminal Attrave (a,)	73166	\$3344		7.00				3.052				4.795R	4.1633	4, 1633		4.7958		
1	 4 <u>]</u>	3,42910	3,42910	+-	5 F	··			2.09711				251547	2,11323	2.09711		2.90327		
-	i] &	2,53685	2,91547	i i	9				2.09771				100	2,91547	2,91547		1,90327		
Alems of Augle		". XHZ	N.J.17	Methylone	A SHC H	בנ"נ"ני		H,2,,12	Mate!	7.7.77	ZC,C,H	7,5,5,7	ن ا.	L',C',H	H'J".17		حريري. سان	* C'C'C'	

SULFIDES $(C_n H_{2n+2} S_m, n = 2,3,4,5...\infty)$

The alkyl sulfides, $C_n H_{2n+2} S_m$, comprise two types of C-S functional groups, one for t-butyl groups corresponding to the C and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each C-S group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243), c_2 in Eq. (15.52) is one, and the energy matching condition is determined by the C_2 parameter. As in the case of thiols, C_2 of Eq. (15.52) for the C-S-bond MO given by Eq. (15.127) is $C_2(C2sp^3HO to S) = 0.64965$.

The C-S group of alkyl sulfides is equivalent to that of thiols where $E_T(atom-atom, msp^3.AO)$ is $-0.72457 \, eV$ (Eq. (14.151)). The t-butyl-C-S group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle θ ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

over the integer multiple of each $E_D(Gmup)$ of Table 15.156 corresponding to functional-group composition of the molecule. E_{mog} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

unctional Group	Group Symbol
C-S (methyl, alkyl)	C-5 (i)
C-S ((CH3), C-S-)	C-S (ii)
CH, group	$C - H \left(C \cdot H_3 \right)$
CH, group	$C - H \left(C H_2 \right)$
	H)
and (n-C)	(3) ひーひ
CC bond (iso-C)	(2)
CC bond (tert-C)	(a) (J-).
CC (iso to iso-C)	(g) :J-U
C(rat-C)	(e)
Christon	(D.J=.)

				Ξ							
Parameter	Group	Original Surfaces of Surfaces and experimental values of C = S (ii) C - H (CH,) C Group	C-H (CH,)	C-H (CH ₁)	dnoub	C. – C. (8) Group	C-C(b) Group	C~C (c) Group	C − C (d) Group	C-C (e) Group	C~C (f) Group
0 (0,)	1.90975	1,90975	1.64920	1,67122	1.67465	2,12499	2.12499	2.10725	2.12499	2.10725	2.10725
(°u)	1.71455	1,71455	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (A)	1.8 1460	1.81460	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
Exp. Bond Length	(dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	1,107 (C-H propune) 1,117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1,122 (isobutane)	1.532 (propane) 1.531 (butane)	1,532 (propane) 1,531 (butane)	1,532 (propane) 1,531 (butane)	1.532 (propare) 1.531 (butane)	1.532 (propane) 1.531 (butanc)	1.532 (propane) 1.531 (butane)
b.c (a _o)	0.84112	0.84112	1.27295	1,29569	1.29924	1.54616	1.54616	1,52750	1.54616	1.52750	1.52750
,	0.89778	0.89778	0.63580	0.63159	0.63095	0.68600	0.68600	0.68883	0.68600	0.68388	0.68888

Bond							-	,								
			et §	. · · ·	5	Final Total	,1	7	Eradus	$E(C2xp^3)$	θ,	8	θ,	-	ď	
		Bond I	Bond 2	Bond 3	Bond 4	, de 50	(°	(a)	(cv.) Final	(eV) Final	©	E	©	(°)	(°)	_
R-S-R ($C-S$ (i) and (ii))	٠,	-0.36229	-0.36229		۰		1,32010	0.87495	-15.55033		129.96	200	82.63	981	60133	_
H,C, - S - C, H, CH, R	ن	-0.36229	e	٥	•	.141 9779	0.07771	COMMO	10001 21					and the	0.3000	_
H,C,-S-C,H,CH,R		0.46290	a ucus	,	, ,			anced's	-13.1 mark	/1////-	130.79	49.21	53.75	1,12037	0.58518	
(C=8 (0) HC = S=C (CH)	,				-	-15290716	0.91771	0.84418	-16.1172	-13.92636	128.69	51.31	51.57	1.18AB9	0.52765	
(C-N (i) and (ii)	٠٠	-0.36229	-0 72457	-0.72457	-0.72457	-154,15170	17116.0	0.78367	-17.36176	-17.17090	125.97	\$4.03	48,94	1.25430	0.46025	_
C-H (CH,)	ن	.0.92918	c	0	0	-152.54487	17716.0	0.86359	-13,73493	-15.36407	77.69	102.51	41.48	123564	0 18708	_
C-H (CH,)	٠	-0.92918	-0.92918	0	0	-153,47406	17710.0	0.81549	-16.68412	-16.49325	68.47	11.53	35.14	135426	0 20013	
C-H (CH)	ij	-0.92918	-0.9291R	H1620.0-	0	-154,40324	17716,0	0.77247	-17,61330	-17,42244	61.10	118.90	3137	147011	911116	
$H_1^{\mathcal{C}}C_1^{\mathcal{A}}H_2^{\mathcal{C}}H_2^{\mathcal{A}} - (C_1^{\mathcal{C}}C_1^{\mathcal{A}})$	۲.	-0,92918	c	0	o	-132.54487	0.91771	0,16359	-15.75493	-15.36407	6.82	116.18	30.08	1.83879	0.38106	
$H_3C_sC_sH_2CH_3-$ (C-C'(a))	ئ	#16£0,0-	-0.9291K	С		-153,47406	0.91771	0,11549	-16,68413	-16.49325	56.41	123.59	26.06	SONO	0.44117	
n - H2C,C(H2C, - R)HCH2 -	ئ	81626-0-	-0.92918	к1626-0-	c	-154.40324	0.9177	0.77247	-17.61330	17 AD344	01.87					
$(R - H_2C_*(R - H_2C_*)C_*(R^* - H_2C_*)CH_* - R^*$,											n later	8	791761	U.51.38K	
((, -(, (c))	-	X1026.0-	-0.72457	-0.72457	-0.72457	-154.71800	0,91771	0.75889	-17,92866	617,73779	47.21	131,79	21,74	1,95734	0.30570	
$I(C, -C, \{d\})$ $I(C, -C, \{d\})$	ڻ	816 <u>5</u> 6,0.	-0.92918	81626'0-	c	.154,40324	0.91771	0.77247	-:7,61330	-17,42244	48.30	131.70	21.50	197162	0.51388	
$ierK'_{*}(R'-H_{*}C_{*})C_{*}(R'-H_{*}C_{*})CH_{*} - (C-C_{*}(e))$	ڻ	154£1.0°	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	23852.11.	67757.71.	50.04	12.96	23.66	1.94462	0.4929x	
(C-('(h;C,-R')HCH;-	ر:	-0.72457	40.92918	#1420 O-	ㄹ	-154.19863	0.91771	0.78153	-17,40869	.17.21783	32.78	11.11	POPE	1,02443	0.47279	
(C-C, 0)	٠,	-0.72457	-0.72457	-0.72457	-0.72457	.154.51390	17716.0	0,76763	-17.92866	ett 67.77.	30,04	129.96	22.66	1.3446.7	0.4929%	
				1				_	_	_	_	_	-		-	

Table 15.155. The MO to HO intercept geometrical bond parameters of airly sulfides. R. R. R. mon H or alkyl groups. Fr is E. (anni – atom. nxp'.AO).

Bond

Table 15.156. The energy parameters (eV) of functional groups of aikyl sulfides.	irs (eV) of functio	nal groups of alky	/ sulfides.							1000	3,00
Parameters	C_S (i)	(ii)	£	CH,	C-#	C-C(a)	(a) 2-2	(a) (b) (c) (c) (c) (d)	(a) C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-	(e) (J-C)	(1) (2) (3)
	Group	Croup	Group	Group	dnos	dnoro	dnan	doolo	dioni	dion	daylo
· v	-	1	3	7 .	į	1	1	1	1	1	-
n,	0	0	2	-	Q	0	0	0	0	0	0
""	0	С	0	0	0	o	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
.:	0.64965	0.64965	_	-		-	1	1	1	1	
2	-	-	-	1	-	-	ı	-	-	1	1
	_	-	0.91771	17710	0.91771	0.91771	17716.0	17716.0	0,91771	0.91771	0.91771
<i>c</i> ,	٥	0	0	-	-	0	0	0	1	1	0
ر.	2	2	-	-		2	2	2	2	2	2
0,	o	0	3	2	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	5.0	5.0	0.5	0.5	0.5	0.5
(,	0.64965	0.64965	_	-	-	1	1	1	1	1	1
r, (er)	-46.36495	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	7.93551	7.93551	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T' (aV)	12.13899	12.13899	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (aV)	-6.06949	-6.06949	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
B(.10 im) (aV)	0	0	-15.56407	-15.56407	-14.63489	-15,56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
AEntun (wm) (cV)	-0.72457	-0.72457	0	0	0	0	c	0	0	0	٥
Er (10 10) (cV)	0.72457	0.72457	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
Er (11,10) (0V)	-31.63537	-31.63537	-67.69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31,63535
$E_r(atom - atom, msp^*, AO)$ (eV)	-0.72457	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
Er (10) (cV)	-32,35994	-32.35994	-67,69450	-49.66493	-31,63537	-33.49373	-33,49373	-33.08452	-33,49373	-33.08452	-33.08452
ω (10 ¹³ rad/»)	30.5436	8.92777	24.9286	24,2751	24.1759	9.43699	6,43699	15.4846	9.43699	9.55643	9.55643
E_{κ} (aV)	20,10434	5.87641	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E, (aV)	-0.28705	-0.15519	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exm (eV)	0.08146	0.08146 [41]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0,17978 [4]	0.09944 [5]	0.12312	0.12312	0.12312 [2]
E_ (aV)	-0,24632	-0.11446	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
East (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	.0.14803	0.14803	0.14803	0.14803
Er (inne) (cl/)	-32,60626	-32,47440	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Executor to 10) (eV)	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Exemple, 10 10) (cV)	0	0	-13,59844	-13.59844	-13.59844	0	0	0	0	0	0
Entrang (aV)	3,33648	3.20462	12.49186	7.83016	3.32601	4:32754	4.29921	3.97398	4.17951	3.62128	3,91754

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy E see that is subtracted from the weighted sum of the Enline, (ell) values based on composition is given by (15.58).

Total Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond Trail Bond	Formula	OEIR	C-S (i)	ľ	C.H.	(.H.)	Æ	C-C (a)	C-C (a) C-C (b)	C-C (c)	C-C (d)	(a) .CC. (e)	() J-J	L	Calculated	Tomorion	Dallatine Comm
Directly building 1			guoro	Cross							•			, F	Total Bond	Total Bond	
Ethyl methyl stiffed 1 0 2 1 1 672	C;H,S	Dimethyl sulfide	2	0	2	6	-								Energy (eV)	Energy (eV)	
Dirichty and tight Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty studies Dirichty	C,H,C	Ethyl methyl sulfide	-	0	. ~	-						•	•	0	31,65668	31.672	0.00048
Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin Martin M	CHIS	Diethyl sulfide	3	•	. ~	. ~	,		> 0			0	•	0	43.81438	43.848	0.00078
Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supprincipal training Supp	CHIN	Methyl propyi sulfide	7	•	. ~	. ~	· c		> <		۰.	0	0	0	\$5,97208	56.043	0.00126
Buty interface 2 3 6 9 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	λ. N.	Isopropyl methyl suffide	2	0	_		,	• •	,			•	•	0	20726'55	56.029	0.00102
Ethyl proper lattifies 1 1 4 6 68.12978 68.185 Ethyl proper lattifies 1 1 4 6 68.12978 68.185 Ethyl proper lattifies 2 0 2 2 4 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	CHIS	Butyl methyl sulfide	2	0	. 7	;	- c) r	* <	۰.		•	0	0	56.07297	\$6.115	0.00075
Ethyl propyl suffide 1 0 2 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	C,H,S	t-Butyl methyl sulfide	-	-	•		· c	• •	.	5 r	۰.	0	0	0	68.12978	68.185	0.00081
Edyl bispropry latified 2 0 0 1 2 1 1 2 0 0 0 0 0 0 0 0 0 0 0 0	CHIS	Ethyl propyl sulfide	_	0	. 7				> 0	٦,	0	•	0	7	68.28245	68.381	0.00
Discoprocyl stiffs 2 0 4 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	CHIS	Ethyl isopropy) sulfide	7	•		. ~		٠.			•	0	٥	0	68.12978	68,210	0,00117
Darry tarly suffice 2 0 0 0 0 0 0 0 0 0	STHO	Ditsopropyl sulfide	7	0	4		٠,	- c	7 -			0	0	0	68.23067	68,350	0.00174
Nettly bluny salitie 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	C,H,S	Butyl ethyl suffide	~	٥	7	. •	+ c		7 (> 0		0	0	0	80.48926	80.542	0.00065
Dibuyl saffide 2 0 2 6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	C,H,,S	Methyl pontyl sulfide	7	٥	. 7			, ,	.	- (۰,	0	•	0	80.28748	80,395	0.00133
Discharge training 2 0 4 2 2 2 4 0 0 0 0 0 104,8045 104,701 Discharge training 2 0 0 0 0 0 0 104,8045 104,701 Discharge training 2 0 0 0 0 0 0 0 104,8045 104,701 Discharge training 2 0 0 0 0 0 0 0 0 104,8045 104,701 Discharge training 2 0 0 0 0 0 0 0 104,8045 104,700 Discharge training 2 0 0 0 0 0 0 0 0 104,8045 104,700 Discharge training 2 0 0 0 0 0 0 0 124,8145 118,9195 118,9195 118,9195 118,9195 118,9195	S.H.S	Dibutyl sulfide	~1	٥	~	ve				> 0	5 (0	0	0	80.28748	80,332	0.00056
Di-buyl stiffs 0 2 6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	SH'IS	Di-sec-butyl sulfida	2	٥	-	. ~			•		.	0	0	0	104,60288	104,701	0.00094
Dissolvely surfide 2 0 4 2 2 0 0 0 0 0 0 0 104,720 Dissolvely surfide 2 0 4 4 4 5 9 9 0 0 0 0 0 123,9138 128,919	Z X	Di-t-buryl suffide	0	7	•			• c	• 0	۰.	5 (0	•	0	104.80456	104.70	-0.00059
Dipenyl sulfide 2 0 2 8 0 8 0 0 0 0 0 0 0 0 0 0 0 0 0 0	C,H,95	Diisobutyl sulfide	~	٥	4	۰,۰) r	,	> 4	ه م	5 (0	0	-5	104,90822	104.920	0.00031
Disoperately sulfities 2 0 4 4 5 9 0 0 128.91828 128.979	Claff _{ES}	Dipentyl sulfide	C 3	0	7		• =		3 6	= 0			0	•	104,74800	104,834	0,00082
	ClaHaS	Disopertyl sulfide	m	0	•	. 4				۰ د		a	0	o	128.91828	128.979	0.00047

												,			
Exp. 6		99,05 (dimethyl sulfide)	97 (ethyl methyl sulfide)	114.0 (ethyl methyl sulfide)	107 (propane)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (burane) 111.4 (isoburane)	109.3 (dimethyl sulfide) 110 (ethyl methyl sulfide)			110.8 (isobulane)		111.4 (isobutane)	F11.4 (isobutane)	
(S)	1	99.06	97.04	114.27	108.44	110.49	110,49	109.50	109.44	109.44	110.67	110,76	111.27	72111	107,50
e. €															
i ₆ (e)															
ø, ©					.	69.51	69,51		70.56	70.56					72.50
£r (eV)		-1.85836	-1.83836	-0.72457	0			B			-1.85836	0	0	-1.83836	
75"		0,84418	0.83954	0.74282	1.15796			35725			0.81549	1.04887	1.04887	1,04887	
ีน . 		-	-	-	a.75		, ,	0.75			-	6,75	0.75	6.75	
5		-	-	0.64965 (Eq. (15.127))	-			1			-	-	•	-	
5		-	-		-			-			-	0.75	0.75	0.75	
C ₁		0.84418	0.81549	0.83600	-	-		-			0.81549	0.91771	17716	0.91771	
C ₁		0.84418	0,66359	0.64965 (Eq. (15.127))	0.86359			0.86359			0.81549	0,87495	0.87495	0,87495	
Atom 2 Hybridization Designation	(Table 15.3.A)	=	25	. \$1	Ħ			ж			23	-	,	1	
Contraction Advant 2		-16.11722	nethylene	-16.27490	т			Ŧ			-16 68412 C,	-14.82575 C _k	-14,82575 C.,	-14.82575 (°,	
Atom I Hybridization Designation	(Table 15.3.A)	11		v	^			,			23	۶	\$	₹.	
E'mbarkt Atom I		-16.11722	.15.75493 methyl (.,	-10.36001	-15.75493			-15.75493			-16.08412 C ₁	.15,55033 C.	-15.55033 C ₅	-15,55033 C.	
2C' Tentinal Atoms	(%)	5.2173	5,1381	5.3364	3,4252			3.4252			4.795	4,1633	4.1633	4.7958	
2c' Bond 1 (0,)		3.42910	3,42910	2,91547	211106			209711			2,01547	2,11323	2.0971.1	2.90327	
(g. 12)		3,42910	3,42910	3.42910	211106			200711			2.91547	2,91547	. 2.91547	72606.7	
Name of Archie 2c' 2c' 2c' L'inhafe Hybridization (verment Hybridization Area Designation (vg) (vg) (vg)		C-S (i))	(C - S (I))	C5 (ii)	H, ZHC, H	לכ"כ"כ"	H'J'J7	Mashyi ZHC, H	70,07	H'.5'.37	່ວ <i>ູ</i> ເດີດ. ເພດ	7C,C,H	#'5'57 ₩'5'57	"3 to 1	75'5'57'

DISULFIDES $(C_n H_{2n+2} S_{2n}, n = 2,3,4,5...\infty)$

The alkyl disulfides, $C_nH_{2n+2}S_{2m}$, comprise C-S and S-S functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each C-S group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulfides, C_2 of Eq. (15.52) for the C-S-bond MO given by Eq. (15.127) is $C_2(C2sp^3HO\ to\ S)=0.64965$ and 15 $E_T(atom-atom,msp^3.AO)$ is $-0.72457\ eV$ (Eq. (14.151)).

The S-S group is solved as an H_2 -type-ellipsoidal-MO that is energy matched to the energy of sulfur, $E(S) = -10.36001 \ eV$, such that $E(AO/HO) = -10.36001 \ eV$ in Eq. (15.42) with $E_T(AO/HO) = E(AO/HO)$. The S-S-bond MO is further energy matched to the $C2sp^3$ HO of the C-S-bond MO. C_2 of Eq. (15.52) for the S-S-bond MO given by Eq. (15.127) is also $C_2(C2sp^3HO\ to\ S) = 0.64965$. In order to match $E_T(atom-atom,msp^3.AO)$ of the C-S group $(-0.72457\ eV)$ (Eq. (14.151)), $E_T(atom-atom,msp^3.AO)$ of the S-S-bond MO is determined using a linear combination of the AOs corresponding to $-0.72457\ eV$ and $0\ eV$ in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is $E_T(atom-atom,msp^3.AO) = -0.36229\ eV$.

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given

in Table 15.163 was calculated as the sum over the integer multiple of each $E_D(G_{mnp})$ of Table 15.162 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

Functional Group	Group Symbol
5-3	C-3
5.5	5-5
CH, group	$C = H(CH_s)$
CH, group	$C-H$ (CH_{z})
3	H-7
CC bond (n-C)	(ز – ز (a)
CC bond (iso-C)	(a) U-U
CC bond (tert-C)	. (a) U=U
CC (iso to iso-C)	(p) U-U
CCUBIC	(e) U-U
CC (to iso-C)	€ U-0

maneter	0-2(3)	515	(×) × -)		C-H	(E) ()-()	(a)	(e) (-)	(g) U-U	(E)	(C)
_	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Quand
(e)	1.90975	2.37173	1.64920		1.67465	2.12499	2,12499	2.10725	2.12499	2.10725	2.10725
(°	1,71455	1,91070	1.04856	1.05553	1.05661	1.45744	1.45744	1,45164	1.45744	1.45164	1,45164
Bond Length L' (A)	1.81460	2.02220	1.10974	1,11713	1,11827	1.54280	1.54280	1.53635	1,54280	1.53635	1.53635
9. Bond	1.816 (dimethyl disulfide)	2.029 (dimethyl disulffde)	L.107 (C - H propano) 1.117 (C - H busane)	1.107 (C - H propane) 1.117 (C - H butane)	1.122 (isobutone)	1.532 (propeno) 1.531 (butene)	1,532 (propane) 1,531 (butane)	1.532 (propano) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1,532 (propane) 1,531 (butane)	1.532 (propane) 1.53) (butane)
),c (a,)	0.84112	1,40510	1.27295	1.29569	1.29924	1.54616	1.54616	1,52750	1,54616	1.52750	1.52750
9	0.89778	0.80562	0.63580	0.65159	0.63095	0.68600	0.68600	0.68888	0.68600	0,68888	0.68888

683

	-	_		7	E,	Final Total	3	,	Ernelmen	E(C.210)	.0	9	,	,	
	 .	Bond 1	(eV) Bond 2	(cV) . Bond S	(cV) Bond 4	Energy ('2sp)	(e)	(6)	Firs (. C	5 O	. C	e' (e'	ė' (e
RS-SR						GA)									
(C - S (i) and (ii))	٠	-0.56229	-0.18114	۰	-		1,32010	0.81527	-15,36918		N.N.	85.73	38,93	1,84513	0.06358
1,50 = 35 = C, M; CM; K	4	-0,36229	-	С	٥	K2772,181.	0.91771	0.89582	-15.18804	-14.99717	130.79	19,21	\$3.75	1 17037	0.58510
(C - N (i))	٠:	-0.36229	*1626'0*	•	•	-152.90716	17719.0	0.84418	-16.11722	-15.92636	121.69	IFIS	\$1.57	1 16679	0.4346
	ن	-0,36229	-0.72457	-0.72457	-0.72437	-154.15170	0.91771	0.78367	-17 36176	0002171	134.07	20.00			
('-H (CH,)	ن	40,92918		۰	٥	143 54487	121.00	2,000		200	600	X.03	48.94	1.25430	0.46025
('-H (CH,)	ļ.	#10COO-	21000				1// (27)	U.Mb.339	-15,75493	-15-36407	77.49	102.51	41.48	1,23564	0.18708
(-H (CH)	. . -			,	5	-133,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	135416	0.22933
H.C. H.C.H.	-	#1476'n-	-0.92918	-0.9291#	٥	-154,40324	0.91771	0,77247	-17.61330	-17.42244	61.10	118.90	31.37	1,42988	937336
(('-(: (a))	ن'	-0.9291R		•	•	-152.54487	17116.0	0.86359	.13.75493	15.56407	63.82	116.18	30.08	1,83879	Agisto
H,C,C,H,2CH,2	ئ ^ع	N1026'0-	1162670-		۰	-153,47406	0.91771	0,81549	21779991-	ACTOL 21.	159				
R-H,C,C, (H,C,-H)HCH,-											i Sar	103%	20.05	0.30830	0.45117
(cc. (b))	٠.	.0.92918	-0.92918	4,92918	c	-154.40324	0.91771	0.77247	-17.6(330	-17,42244	6,3	131.70	21.90	D)176.1	0.51348
$R - H_1C_1(R' - H_1C_2)C_2(R'' - H_2C_2)CH_2 - (C' - C'(0))$	<u>ر</u>	41.929.1K	-0.72457	-0,72457	-0 72457	-154,71160	17716.0	0.75KBD	-17.72866	יתנת.דו-	45.21	131.79	17.7	750	6565
$lsuC_sC_s(H_sC_s-R)HCH_s-$ $(C-C_sC_d)$	ڻ	-0.9291ж	-0.92918	-0.9291K	e	-154.40324	17716.0	CMTT.0	-17.61330	-17,42244	8	131.70	2.00	9	2000
$(eH_{a}^{\prime\prime}(R-H_{2}C_{a})C_{a}(R-H_{3}C_{a})CH_{2}-(C-C_{a}C_{b})$	ڻ	-0.72457	.0.72457	-0,72457	.0.72457	-[54,5 399	177160	0,76763	-17.92866	-(7,73779	X 28	129.56	266	978	90000
$IariC_{\mu}C_{\mu}(H_{\mu}C_{\mu}-R_{\mu})HCH_{\mu}-(C_{\mu}-C_{\mu}(R))$	ť	-0.72457	-0.92918	-0.92918	ė.	-154.19863	17716,0	0.78155	-17.40869	S#12.71-	17.73	27.11	26.2	196	
$(C-C, (R-H,C_s)C, (R-H,C_s)CH_s - (C-C, (0))$	ڻ	-0.72457	-0.72457	-0.72457	-0,72457	-154.5(399	177160	0.76765	27802 71.	91111					411111
								!		-	3	129.96	72.66	1.94462	Q.49298

Table 13.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides. R. H. R. are 11 or alkyl groups. E., is K., ann. – ann., mrp. AO. Bond

Aron F. K. Aron F. K. Aron F. K. Aron F. K. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron F. Aron

	Graup	Group	C'H',	C.H.	Group	Grade Grade	C-C(b)	ر-(د) Group	C-C (d) Group	C-C (e)	() 2-C
"a"	-		۳	7	-	-	-		-	-	-
n,	0	o	7	-		0	0	٥			- -
'n	0	٥	0		0	0	0	°			,
<i>C</i> ,	0.5	5.0	0.75	0.75	0.75	0.5	0.5	5.0	50	Ì	,
	0.64965	0.64965	-	-	-	-	-	_	-	} -	3 -
c'	-	-	-	-	-	-	_	-	-	. -	-
£3	1	-	0.91771	17116.0	0.91771	0.91771	0.91771	0.91771	0.91771	122100	0.01771
6,3	0	С	0	-		0	0	0	_	_	٥
e,	2	2	-	-	-	2	2	2	2	2	-
c,	0	0	m	2	1	0	°	o	0	o	-
a	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	20
2.0	0.64965	0.64965	-	1		-1	-		_	-	-
1', (aV)	-46.36495	-31,74215	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	7.93551	7.12083	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
1 (cr.)	12,13899	0.69177	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V., (cV.)	-6.06949	-3.34589	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3,45250	-3.38732	-3.45250	-3.45250
131.00 mg (dV)	0	-10.36001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-15,35946	-15,35946
Ochina La naj (av.)	-0.72457	٥	٥	. 0	0	0	0	0	0	0	0
(c l m) (cV)	0.72457	-10,36001	-15.55407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-13.56407	-15.35946	-15,35946
Fr (n,ten) (aV)	-31.63537	-31,63544	-67,69451	-49,66493	-31,63533	-31,63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
ET (Olimi - alam, ninp' A() (eV)	-0.72457	-0.36229	0	0	۰	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
F. [w] (cV)	-32.35994	-31.99766	-67.69430	-49,66493	-31,63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
a) (10" rad/s)	30.5436	6.45076	24,9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
E, (eV)	20,10434	4.24600	16.40846	15,97831	15,91299	6,21159	6.21159	10.19220	621159	6.29021	6 2007
E, (eV)	-0.28705	-0.13044	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	0.16416	-0.16416
Figure (eP)	0.08146	0.06745 D	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0,09944	0.12312	0.12312	0.12312
E. (cV)	-0.24632	-0.09672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
Cytimes (CV)	-32.60626	-32.09437	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
1: " (c. 10.10) (c. V.)	-14,63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14.63489
E (-) (-1/2)	D	0	-13,59844	-13.59844	-13,59844	٥	0	0	0	۰	0
لا اربسدا (دیر)	3.33643	22760	20107 CT								

Table 13.143. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 13.162 compared to the experimental values (3). The magnetic energy E_{acc} that is subtracted from the weighted sum of the $E_{acc} | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | barrel | b$ C-C (e) (p) 2-2 C-C (a) C-C (b)

_										~	~~	$\neg \tau$					
	6.i.6			(dinether disside)	(dimethyl disalGds)	103.2 (dimethyl disulfida)	107 (propuse)	112 (progate) 113.1 (butanc) 110.8 (isobutano)	111.0 (butme) 111.4 (isotutane)				110,8 (isobulane)		111.4 (fsobstanc)	11 L.4 ((sobutane)	
	j =	3	109.50	109.44	7111.77	103.57	10%.44	110.49	110.49	109,30	109,44	109.44	110.67	110.76	111.27	ti1.23	107.50
	ø" ;	ေ															
	6	©														ļ	•
1	<i>o</i> , :	<u> </u>		70,56				42.51	69.31		70.56	70.56					72.50
40).	ᆈ	(e,)	c		a	-0,72457	0			0			-1,85836	۰	o	-1,85834	
ı — аюнтизр ^э .	٧,		1.15796		970110	1981.0	1.157%			1,15796			6,81549	1.04887	1,04887	1.04887	
E, is E, aton	ن		0.75		6.7.5	-	0.75			67.0			-	0,73	67.0	0.75	
o were used	ᢐ		-		0,76144 (Bq. 15.126))	0,64965 (Eq. (15.127))	-			-			-	-	-	-	
receding angl	ر ان		-		87.0	-	-			-				87.0	82.0	0.73	
ers from the p	5	Alem 3	-		0.76144 (Eq.(15.126))	17719.0	-			-			0,815d9	177160	17716.0	1723670	
, the paramet	5	Alon I	0.16359		0.87405	0.64965 (Eq. (13.127))	0,86359			0,86359			0,81549	0,87495	0,87495	0,87495	
e calculation of 6	Atom 2 M-heiderstless	Designation Table (\$ 3.4)	H		5	-	±			Ŧ		}	a	-	-	-	
ics [1]. In th	Eneme	Albre 2	=		1038601.	-14,82575	I			=			-16.63412	-14.83573 C.,	-14.12575	-14,12575	
xperinental valu	Alom I	Hybridization Designation	11886 23.61		s	v	,			1			SZ	77	~		
ifides and	Er	į	.15 75693		-15,55033	10095.01-	.15,73403			.13.75493			-16.68412	-15,55033	-13,33033	-15.55033	
f alkyi disu	72	Aires	2.05		4,6228	5.701.2	1,4251			3 4252			4.7958	4.1633	£(1633	4.705#	
traneters o	26.	<u>;</u> (°	2191711		3,42910	3,42910	2.11106			2,09711			2,91547	2,11323	117711.5	2,90327	
and angle pre	75.] §	111001		200711	3 82666	2,11106			1.09711			291547	2,91547	1915.7	2.90327	
Table 15 164. The bond angle parameters of allyst disulfides and experimental values (1). In the calculation of $ heta$, the parameters from the preceding angle were used. E, is E, {atom - atom, may AO},	Appear of Augle		777.77	1000	ZHC, S	Z.N.C.	Methykne /HC H	'קב'ניני,	Н.С.И	Medical Market	33.1	H.J. 37	20,00	H*.7.77	K, C, H	4.7.2	

SULFOXIDES
$$(C_n H_{2n+2}(SO)_n, n = 2,3,4,5...\infty)$$

The alkyl sulfoxides, $C_n H_{2n+2}(SO)_m$, comprise a C-SO-C moiety that comprises C-S and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur 15 atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the S AO has an initial energy of $E(S) = -10.36001 \, eV$ [38]. To meet the equipotential condition of the union of the $S = O H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the S = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771)$$

$$= 1.20632$$
(15.128)

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two C-S groups. The formation of these bonds is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement:

where the quantum numbers (ℓ, m_{ℓ}) are below each electron. The 3s shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}(S, 3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is $-11.57099 \ eV$. Using Eq. (15.16) with the radius of the sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}(S3sp^3)$ and E(magnetic):

$$E(S3sp^{3}) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{3sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r_{16}^{3}}$$

$$= \frac{-e^{2}}{8\pi\epsilon_{0}1.17585a_{0}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(1.32010a_{0})^{3}}$$

$$= -11.57099 \ eV + 0.04973$$

$$= -11.52126 \ eV$$
(15.130)

Then, the hybridization energy $E_{hybridization}(S3sp^3)$ of the $S3sp^3$ HO is

$$E_{hybridization}(S3sp^{3}) = E(S3sp^{3}) - E(S)$$

$$= -11.52126 \ eV - 10.36001 \ eV$$

$$= -1.16125 \ eV$$
(15.131)

The SO group is matched to the C-S group with which it shares the common 10 hybridized S atom. Consequently, $E_{hybridization}(S3sp^3)$ is subtracted from $E_T(Group)$ in the determination of $E_D(Group)$ (Eq. 15.56)). Furthermore, the energy of the S=O-bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E(AO/HO) = E(S3sp^3) = -11.52126 \, eV$ and $E_{H_2MO}(AO/HO) = E_{hybridization}(S3sp^3) = -1.16125 \, eV$. Then, $E_T(AO/HO) = E(S) = -10.36001 \, eV$. Also, $E_T(atom-atom,msp^3.AO)$ of the S=O bond is zero since there are no bonds with a $C2sp^3$ HO.

The C-S group is solved as an energy minimum by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four S3p electrons to form a $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}(S3sp^3)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$ -shell hybridization factor, $c_2(S3sp^3)$, is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045$$
 (15.132)

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the 5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E(S3sp^3) = -11.52126 \, eV$ (Eq. (15.130)). To meet the 10 equipotential condition of the union of the C-S H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}\left(0.85045\right) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0 \quad \text{and} \quad E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO). \quad \text{For sulfoxides},$ $\Delta E_{H_2MO}(AO/HO) = -0.72457 \ eV. \quad \text{Further equivalently},$ $E_T(atom-atom, msp^3.AO) = -0.72457 \ eV \quad \text{(Eq. (14.151))}.$

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each E_D(Granp) of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	C-S
SO	SO
CH ₃ group	$C-H$ (CH_3)
CH₂ group	$C-H\left(CH_{2}\right)$
СН	<i>C</i> – <i>H</i>
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

1.42988

Q.15329 Q.07304 Q.53472 Q.53026 Q.14708 Q.29933 Q.37326

1.5642 1.50400 1.11799 1.09461 1.15245 1.23564

(o) 'q'

0,45117

0.51388

0.51388

0.47279

1								Π
	(a) 2→2	Group	2.10725	1.45164	1.53635	1,532 (propane) 1,531 (burane)	1.52750	0.68888
	(a) 2-2	Стоир	2.10725	1.45164	1.53635	1,532 (propane) 1,531 (butane)	1.52750	0.68888
	(p)) –)	Group	2.12499	1,45744	1.54280	1.532 (propane) 1.533 (burane)	1.54616	0.68600
	(a) 2-2	Group	2,10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
	(Q) ()-()	Group	2.12499	1.45744	1,54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
	(a) .))	Group	2.12499	1.45744	1,54280	1,532 (propane) 1,531 (butane)	1.54616	0.68600
	C-H	Oroup	1.67465	1.05661	1.11827	1.122 (isobutane)	1,29924	0.63095
.s [1].	(-H (CH.)	Group	1.67!22	1,05553	1.11713	1.107 (C - H propane) 1.117 (C - H butane)	1.29569	. 0.63159
lers of alkyl sulfoxides and experimental values [1].	('~# (r#,) Group		1.64920	1.04856	1,10974	1.107 (C-H propane) 1.117 (C-H butane)	1.27295	0,63580
eters of alkyl sulfoxides and	os	Group	1,98517	1,40896	1.49118	1,485 (dimethyl sulfoxide)	1,39847	0,70974
able 15.166. The geometrical bond paramet	C-5	Group	1.87325	1.67271	1.77031	l. 799 (dimethyl sulfoxide)	0.84328	0.89294
Table 15.166.	Parameter		(°0) v	c. (u°)	Bond Length 2c' (A)	Exp. Bond Length (A)	b,c (a,)	,

		-	<u>.</u>	d	J	Final Total			Cradont	(7,3,1)	Ġ	96	9
R,S = 0 R,S = 0 R, - 50		(eV) Bond 1	(aV) Bond 2	(aV) Bond 3	(eV) Bond 4	Energy C24p ³ (eV)	(e)	(°)	(eV) Final	(eV) Final	€	Ξ	· C
R ₁ = 50	S	•	-0.36229	-0.36229			1,32010	0.87495	15,35033		87.67	100.22	38.00
R, -50	0		e	0	0		1.00000	0.91771	-14 12575		84.06	95.94	40.75
	S	-0.36220	0.36229	o	0		1,32010	\$6748'D	-13.55033		129.35	50.65	53.36
H,C 5(O) - C,H,CH,R	c,	-0,36229	c	0	0	451.9779M	17116.0	0.89582	-15.11804	-14.99717	130.19	18'69	54.24
H,C, -S(O)-C,H,CH,R	ť	-0.36229	-0,92918	0	0	-152,90716	17716.0	0,84418	-16.1:722	-15.92636	128.05	51.95	52.03
C-H (CH,)	υ	-0.92918	0	0	0	-152.54487	12410	0.86359	-15.75493	-15.56407	47.77	102.51	41.43
C-H (CH ₂)	Ĺ	0.92918	-0.92918	۰		-133,47406	17716.0	0.81549	-16.68412	-16,49325	(R.47	111.53	33.84
C-H(CH)	i	XIGZ6'O	.0.9291R	-0.93918		-154.40324	17712.0	0.77247	-17.61330	-17.42244	61.10	118,20	31.37
H,C,C,H,CH,	5.	-0.9291R	٥	Ü	a	-152.54417	177160	0,86359	-15.75493	-15,36407	21.ED	116.18	30.01
H,C,C,H,CH, (C,-C'(a))	U*	-0.9291A	81626.0-	c	0	-[53,47406	14716.0	0,81549	-16 61412	-16.49325	I≯′95	92.551	26.06
	U ^d	40.92918	81620,0-	#1626'D+		-154.40324	17710.0	0.77247	-17.61330	17.42244	48.30	131.70	21.90
$n - H_2C_s(R - H_2C_s)C_s(R^* - H_1C_s)CH_1 - (C - C_1C_1)$	ن	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	17160	0,75889	17.92866	67.57.71-	48.21	131.79	11.74
(C-C, (d))	Ů.	-0,9291#	N1020.0.	81929.0-	e	-154.40324	17710.0	0.77247	-17.61330	-17.42244	48.30	131.70	21.90
$(enC_{*}(R'-H_{!}C_{*})C_{*}(R''-H_{!}C_{*})CH_{!}-(C_{!}C_{!})$	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	017.77.71	\$0.04	129.96	22.66
ן ופונר,"כ; (H,C, - R') HCH, -	C,	-0.72457	-0.92918	-0.9291#	ė	-154.19163	17710,0	0.78155	-17.408.69	-17,21783	52.78	127.23	24,04
(C-C (t) ποC*(R'-H-C*)C*(R''-H-C*)CH*-	ئ	-0,72457	-0.72457	-0.72457	-0.72457	-154.51399	17710.0	0.76765	99826-71-	0.77.71.	\$0.04	129.96	27.66

						,			47.2	1300	
Parameters	Graup Graup	Group	Croup	Group	Group	Good	Group	Group	Group	Group	Group
n,	-	2	5	2	-	-	1	1	1	-	1
n,	0	0	7	-	0	0	0	0	0	0	0
'n	0	0	0	0	0	0	0	0	٥	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	5.0	0.5	0.3	0.5	0.5
	0.66951	-	-	-	-	-	-	-	1	1	1
5	-	_	-	-	-	_	_	-	1	1	-
	-	1.20632	17110	14416.0	0.91771	0.91771	0.91771	0.91771	17716.0	17716.0	17716.0
	0	0	0	-	1	0	0	0	1	1	0
	2	•	-	-	-	2	2	2	2	2	2
5	0	-	6	2.	_	0	0	0	0	0	0
	5,0	9.5	0.75	0.75	0,75	0.5	0.5	5'0	0.5	0.5	0.5
.,	0.66951	-	_	-	-	1	-	-	1	1	-
V, (eV)	46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
V, (aV)	8.13401	19,31325	38.92728	25.78002	12.87680	9.33352	9.33352	9,37273	9,33352	9.37275	9,37275
F (aV)	12.47306	20.81183	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6,90500
7.(5.)	-6.23653	-10.40592	-16.26957	-10,53337	-5.24291	-3.38732	-3.38752	-3.45250	-3.38732	-3,45250	-3.45250
l: (.m un) (eV)	0	-11.52126	-15,56407	-15.56407	-14.63489	-15,56407	-15,56407	-15,35946	-15.56407	-15,35946	-15.35946
ΔΕ _{11,10} (20 m) (2V)	-0.72457	-1.16125	o	0	Б	0	0	0	0	0	0
157 (see 110) (aV)	0.72457	-10.36001	-15.56407	15.56407	-14.63489	-15.56407	-15,56407	-15,35946	-15,56407	-15,35946	-15.35946
(c) (c)	-31.63521	-63.27088	-67.69451	-49,66493	-31.63533	-31.63537	-31,63537	-31,63535	-31,63537	-31.63535	-31.63535
$E_T \left(\sigma t n m - \sigma t \sigma m, n \kappa p^2, AO \right) (cV)$	-0.72457	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1,44915
Er (120) (cV)	-32,35994	-63.27074	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
a (10" rad/s)	30,8880	17,6762	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9,55643	9.55643
Er (0V)	20.33104	11,63476	16,40846	15.97831	15,91299	621159	621159	10.19220	6.21159	6.29021	6.29021
E. (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Erm (aV)	0.08543	0,12832	0.35532 (Ea. (13.458))	0,35532 (Eq. (13,458))	0,35532 (Eq. (13,458))	0.12312 f2]	0.17978	0.09944	0.12312	0.12312	21221.0 [2]
En (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (cV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
External (cV)	-32.60589	-63.56937	-67.92207	-49,80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33,18712	-33.18712
E may (e to 110) (eV)	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
Emen les en int (eV)	0	-1.16125	-13.59844	-13,59844	-13.59844	0	٥	٥	0	٥	0
(E. (nue) (cV)	3,33611	3.86856	12.49186	7.83016	3,32601	4,32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table (5,169, The total bond energies of alkyl suffixides calculated using the functional group composition and the energies of Table (5,168 cumpared to the experimental values [3].

Formula Name C-C (a) C-C (b) C-C (d) C-C (d) C-C (e) C-C (d) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-

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	Cal. 0	<u> </u>	96.20	106.48	108.t	110.49	110.49	10) 50	109.44	109.44	110,67	110.76	111.27	111.27	
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rom the preced	2	Alon 3	0,12552	0.05375 (Eq. (15.?14))	-			•			arstro	17716.0	(17719,0	0.91771	
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enimental values (Atom Hybridization	Designation (Table 15.3.A)	17	7	,			7			ы	3	۶.	ક	
ides and ext	Erre	Alma I	1647951	-15.14804 C.	-15.75493			-15.75495			-16.6B412	-15.55033	*,) ::afr'fi-	-15.55033 C',	
alkyi suifox	76.	νρ (υ°)	4.9800	4,9598	3,4252			3,4352			4.795K	4.1633	4.1633	4,7958	
rameters of		(4)	334541	2,81792	2,11104			2,09711			2,91547	2,(1323	2.09711	2,903,27	
and angle pa	::]	(%)	3,3454!	3,34541	2,11,06			2,09711			2,91547	2.91347	2.91547	2.90327	
Table 15,770. The borned angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of \$0., the parameters from the proceeding single were used. \$\overline{E}_i\$ is \$\overline{E}_i\$ (non-oton, map 'AO)	Alons of Asplo		*.x'.77	0K*37	Makstone LHC, H	תנ'נ'נ'	H"S"S	H. JH.Z	ע. ניני. מי	H'J',)7	۵۰ ر حرد کر تارم میران	"," H ""," H	ZC,C,H In (',	מט נ" קצ"נ"נ"	7.7.7

SULFOXIDES
$$(C_n H_{2n+2}(SO)_n, n=2,3,4,5...\infty)$$

The alkyl sulfoxides, $C_n H_{2n+2}(SO)_m$, comprise a C-SO-C moiety that comprises C-S and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur 15 atom is energy matched to the $C2sp^3$ HO. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the S AO has an initial energy of $E(S) = -10.36001 \, eV$ [38]. To meet the equipotential condition of the union of the $S = O H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the S = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(0 \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771)$$

$$= 1.20632$$
(15.128)

The S atom also forms a single bond with each of the $C2sp^3$ HOs of the two C-S groups. The formation of these bonds is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement:

25
$$\frac{3sp^{3} \text{ state}}{\uparrow} \qquad \uparrow \qquad \uparrow \qquad \uparrow \\ 0,0 \qquad 1,-1 \qquad 1,0 \qquad 1,1$$
 (15.129)

where the quantum numbers (ℓ, m_{ℓ}) are below each electron. The 3s shell remains unchanged. Then, the Coulombic energy $E_{Coulomb}(S, 3sp^3)$ of the outer electron of the $S3sp^3$ shell given by Eq. (15.118) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is -11.57099~eV. Using Eq. (15.16) with the radius of the sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell is given by the sum of $E_{Coulomb}(S3sp^3)$ and E(magnetic):

$$E(S3sp^{3}) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{3sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r_{16}^{3}}$$

$$= \frac{-e^{2}}{8\pi\epsilon_{0}1.17585a_{0}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(1.32010a_{0})^{3}}$$

$$= -11.57099 \ eV + 0.04973$$

$$= -11.52126 \ eV$$
(15.130)

Then, the hybridization energy $E_{hybridization}(S3sp^3)$ of the $S3sp^3$ HO is

$$E_{hyhridization}(S3sp^{3}) = E(S3sp^{3}) - E(S)$$

$$= -11.52126 \ eV - 10.36001 \ eV$$

$$= -1.16125 \ eV$$
(15.131)

The SO group is matched to the C-S group with which it shares the common 10 hybridized S atom. Consequently, $E_{hybridization}\left(S3sp^3\right)$ is subtracted from $E_T\left(Group\right)$ in the determination of $E_D\left(Group\right)$ (Eq. 15.56)). Furthermore, the energy of the S=O-bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that $E\left(AO/HO\right) = E\left(S3sp^3\right) = -11.52126 \, eV$ and $E_{H_2MO}\left(AO/HO\right) = E_{hybridizotion}\left(S3sp^3\right) = -1.16125 \, eV$. Then, $E_T\left(AO/HO\right) = E\left(S\right) = -10.36001 \, eV$. Also, $E_T\left(atom-atom,msp^3.AO\right)$ of the S=O bond is zero since there are no bonds with a $C2sp^3$ HO.

The C-S group is solved as an energy minimum by hybridizing the 2s and 2p AOs of the C atom to form a single $2sp^3$ shell and by hybridizing the four S3p electrons to form a 20 $S3sp^3$ shell, and the sharing of electrons between the $C2sp^3$ HO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the $S3sp^3$ shell, $E_{Coulomb}(S3sp^3)$ given by Eq. (15.120) in Eq. (15.63), the $S3sp^3$ -shell hybridization factor, $c_2(S3sp^3)$, is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045$$
 (15.132)

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the 5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 parameter. In alkyl sulfoxides, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the $S3sp^3$ HO has an energy of $E(S3sp^3) = -11.52126 \, eV$ (Eq. (15.130)). To meet the equipotential condition of the union of the C-S H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor C_2 of Eq. (15.52) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951\ \ (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in Eq. (15.42) with $E(AO/HO) = 0 \qquad \text{and} \qquad E_T(AO/HO) = \Delta E_{H_1MO}(AO/HO). \qquad \text{For sulfoxides,}$ $\Delta E_{H_2MO}(AO/HO) = -0.72457 \, eV. \qquad \qquad \text{Further} \qquad \text{equivalently,}$ $E_T(atom-atom, msp^3.AO) = -0.72457 \, eV \quad \text{(Eq. (14.151))}.$

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each E_D (comp) of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	C-S
SO	SO
CH₃ group	$C-H$ (CH_3)
CH ₂ group	$C-H$ (CH_2)
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C) - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	C-C (e)
CC (t to iso-C)	C-C (f)

Parameter											
	Group	Group	('-'H (CH',)	C-H (CH ₁)	C – H Group	CC. (a) Group	. CC (b)	C-C(c) Group	C-C (d) Groun	(c) (c)	() U-U-U
a (a,	1.87325	1,98517	1.64920	167122	1 67464	1 13400	2005			design	drop
(3)	177731	1 40904				£.15139	2,12499	2.10725	2.12499	2.10725	2.10725
Book		0.000.	1.04836	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1.45164	145164
Zc' (A)	1,77031	. 1.49118	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
			107	1 107							
Length	1.799	1,485	H-2)	H-U)		1.532	1.532	1.532	1.532	1.532	1.532
Ē	(dimethyl sulfaxide)	(dimethyl sulfoxide)	propane)	propane)	(isobutane)	(propane) 1.531	(propune)	(propane) 1.531	(propane)	(propane)	(propane)
-			(C-H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(butane)	(hotane)
p.c. (a°)	0.84328	1.39847	1.27295	1.29569	1.29924	1.54616	1 54616	03260	2,2,2		
u	0.89794	710010	003170				200	06/26	0,046,1	1.52750	1.52750
		4.102.14	0.0000	0.031.59	20029	O KOKON	00/07				

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DUOG	Atom	E.	2	. 12		Final Total									ļ
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Ellergy C259] [6]	'§ @	(cV)	E(C2sp²)	è ©	ø- ©	&. ©	(a,)	d _{z.}
R.S. = O						(cV)				Fina			:	:	-
R.S. a.O.	,	0	-0.36229	-0.36229	С		1,32010	0,87495	.15.55033		F7.67	18.13	8:		
S = 80	-		٩	0	٥		1.00000	17716.0	-14.82575		20.73	2	DIT'es	200	0.15529
200	۶.	-0.36229	-0.36229	•	0		1,32010	0.87495	12055 57				6,0	130400	0.00504
H,C, -3(0)-C,H,CH,R	ن	-0.36229	0	D		-151.97708	17716.0	0.82582	-15 IRRO	T14 00717	20.00	30.6	33.36	1.11799	0.55472
H,C S(O) - C,H,CH,R	c,	-0.36229	-0.9291R	۰		-152.90716	122160	0.84418		/I/AC'bla	130.19	49.81	27.75	1.09461	0.57809
C-H (CH,)	١	-0.9201K	0	٥	٥	152 54417	4,60	4000	771170	08020.51	128.03	51.95	52.03	1.15245	920250
C-H (CH ₂)	ŀ	-0.92918	8102G-0-			20121 531		Creme's	-13.13493	-15.36407	77.49	102.31	41.48	1,23564	0.18708
(L-H (CH)	ļ.				,	-133.47406	1416.0	0.81549	-16.61412	-(16,49325	68.47	11.53	33.84	1.35486	0.2033
- K. R. C.		-0.9291K	-0.9291x	-0.92918	o	-154,40324	17710.0	0,77247	-17,61330	-17.42244	61,10	118.90	31.37	1 47988	ACT 0
(C - C (a))	U,	-0.9291#	•	•	•	-152.54487	17710.0	0.16359	-15.75493	-15.36407	63.82	116.18	30 03	626.0	
H,C,C,H,CH, -		#10000 O	2000	ľ										Cape of	oratuo
(C=('(a)) N=H('('(H(C-p))H('))	:		u1676'm	-	٥	-153.47406	0.91771	0.81549	-16.68412	-16.49325	\$6.41	123.59	26.06	1.90890	0.45117
(C-C (b))	ڻ	-0.92918	-0.9291R	#16ZG-0-	•	-154,40324	Q.91771	0,77247	-17,61330	-17,42244	48.30	8,15	8 72	5160	
R-H,C,(K-H,C,)C,(R"-H,C,)CH;-	,	-1000													W31388
(C-C (e))	;	91676.70.	41,72437	-0.75457	-0.72457	-154.7(860	0.91771	0,73889	-17.92866	•17.73.79	48.21	131.79	21.74	M756.1	0.50370
(C-C, (d))	ڻ	N1626'0-	4022018	-0.92918	c	-154.40324	0,91771	0,77247	-17,61330	-17.42244	48.30	£ 15	8		
$lenC_{*}(R'-H_{*}C_{*})C_{*}(R'-H_{*}C_{*})CH_{*} \{C-C^{*}(9)\}$	٠	-0.72437	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76763	-17,92806	97.67.71.	20 55	ě		7	0.51388
wmC,C, (H,C, -R')HCH, -	ن	-0,72457	-0.929/8	A 1000 G	,			†					45.73 17.09	1,54462	0.49298
(soC (R'-HC)C (R'-HC)C'H -	·				5	-124.19803	14116.0	0.78155	-17.40869	-17.21783	52.78	11771	77.00	1,92443	0.47279
(C-C (f)	ئ	-41.72457	-0.72457	-0.72457	40.72457	-154,31399	17716.0	0.7676.3	-17,92866	0.7.7.7.1.	30.04	12.36	22.66	08863	0.40304
							1	Ì	-	-	_	_		-	

Parameters	Parameters C - S Group	SO Group	C.H.	CH; Group	C – H Group	C-C (a) Group	C-C (b)	C-C (c)	C-C (d) Group	(a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	C-C (E) Group
n,	_	2		2	-	,	-	1		1	
u,	0	0	2	_	0	0	0	0	0	0	0
u'	0	0	0	0	0	0	0	0	0	0	0
	0.5	5.0	0.75	0.75	0.75	5.0	0.5	6.0	0.5	0.5	0.5
	0.66951	-	_	1	_	-	1	1	-	-	-
	-	_	-	_	_	-	1	1	1	1	-
	 - 	1.20632	17716.0	17716.0	0.91771	17716.0	17716.0	0.91771	0.91771	17710	17719.0
	٥	0	0	_	-	0	0 .	0	_	1	Û
.5	2	4	-	_	-	2	7	τ	7	7	7
	0	_	3	2	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	50	0.5	5'0
	0.66951	-	-	-	-	_	-	_	-	-	-
1, (ct/)	-46.73032	-82.63003	-107,32728	-70,41425	-35.12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29,10112
V, (vV)	8.13401	19,31325	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9,33352	9.37273	9.37273
T (aV)	12.47306	20.81183	32,53914	21.06675	10.48582	6,77464	6.77464	6.90500	6.77464	6,90500	6.90500
V, (eV)	-6.23653	-10.40592	-16,26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(10 110) (cV)	o	-11.52126	-15,56407	-15.56407	-14,63489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
DE IL IN IN (CV)	-0.72457	-1,16125	0	0	0	0	0	0	0	0	0
Fr (w m) (cV)	0.72457	-10.36001	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
E, (u,sn) (eV)	-31.63521	-63.27088	.67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31,63535	-31,63535
Fr (atom - atom, nisp', AO) (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
Er (see) (eV)	-32,35994	-63.27074	-67,69450	-49.66493	-31.63537	-33 49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
(x/pa, 101) to	30.8880	17.6762	24,9286	24.2751	24,1759	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
Ex (eV)	20.33104	11.63476	16,40846	18,97831	15,91299	6.21159	621129	10.19220	621159	6.29021	6.29021
E, (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16315	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Erm (cV)	0.08543 [42]	0.12832	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.12312 [2]	0.17978	0.09944 [5]	0,12312 (2)	0.12312	0.12312 [2]
E (cV)	-0,24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (cV)	0,14803	0.11441	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
Ey (imag) (cV)	-32,60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
E new la, so m) (eV)	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
Erra le, so m) (eV)	٥	-1.16125	-13.59844	-13,59844	-13.59844	٥	0	0	0	0	٥
E., (may) (cV)	3,33611	3.86856	12.49186	7.83016	3.32601	4.32754	4.29921	3.97998	4.17951	3.62128	3.91734

Table 15.169. The total bond energies of alkyl suifaxides calculated using the functional group composition and the screnges of Table 15.168 compared to the experimental values [3].

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	Εκρ. θ (°)	96.6 (dimethyl rufloxide)	106.7 (dimediyi sulfoxide)	TO! (camedouct)	112 (propane) 113.8 (butane) 110.8 (isobutane)	171.0 (butanc) 111.4 (isobutanc)	110.3 (dimethy! saffoxide)			110.8 (isobutane)		111.4 (isobutant)	111.4 (irobulanc)	
	(S. 6)	94.20	106.89	2	110.49	05,011	05-601	19.60	100.44	19011	110.76	111.27	11127	107.50
	e, C													Γ
	e. O													
	ø, ©				15.00	1509		70.56	70.S6					250
sp'.40).	(eV)	-1.85\$36	-1.65376	o			0			-1.85836			-1,85836	
IRI - COM, DI	v	0.82562	0.87489	1.15796		·	1.15796			0,11549	1.04887	I,04RB7	1,04887	
ir is Er(ala	ď	. 1	1	0.75			6.75			,	0.75	87.0	0.75	
vere used.	<u>ئ</u>	-	-	-			-				-	-	-	
fing angle w	ري ا		-	-	_		-				0.75	Q.75	0.75	
om the preced	C. Airon 3	0.82562	0.83393 (Eq. (15.114))	~			-			OFFIR'O	12216'0	17710.0	17716.0	
parameters fr	C ₂ Alem I	0.82562	0.89582	0,86359			0,86359			0,41549	0,87495	0.87495	0,87495	
sperimental values [1]. In the calculation of $ heta$, the parameters from the preceding angle were used. \mathcal{L}_r is \mathcal{L}_r dann – arom, asp., AO	Atom 7 Hybridization Designation (Table (5.3.A)	=	0	н			н			22	-	_	_	
1]. In the ca	Eradosta Alem I	-16,47951	י טאנואַנוי.	×			н			.16,64412 C,	-14,K2575 C ₄	-14.X2575	-14.x2573 (°,	
crimental values [Atom I Hybridization Designation (Table 15.3.A)	17	2	7			,			25	\$	ş	٠.	
ides and ext	Erratus Alum 1	1864-91-	.15.18804 C,	.15.73493			-15.75493			-16.61412 C.	 -15.55033	-15.55033 f',	-(5.53n33 C.	
alkyl sulfox	2c' f. Torvind Aluny (G ₀)	00%6'≯	4,930µ	1,425		 	3.425.2			4.7058	££71.53	4,1633	H507.F	
rancters of	2c' lbmd 2 (a,)	3,34541	2,81702	2.1110%			2.09741			2.91547	211323	2.00711	2,90327	
ad angle pa	2c' Remi 1 (0 ₀)	3,34541	3,34541	2.11106			2,09711			2.91547	2,91547	2.91547	2.90327	
Table (5.170. The bond angle parameters of alkyl sulfoxides and ex	A battle of Atuation	, Xe.75	US'SD	H.".H7	*.5".57	H*:5°.57	Anathri LHC H	7.7.7.7	H"5",37	47,5',5', to C,	ויי נ" אינ"נ"#	H*, J, 3)7	بيما زي ^م 7ز.'ز.'د	7.7.77

DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle $\theta_{ZS=OICSC}$ between the plane defined by the CSC MO comprising a linear combination of two S-C-bond MOs and a line defined by the S=O-bond MO where S is the 5 central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance d_1 along the bisector of θ_{ZCSC} from S to the internuclear-distance line between C and C, $2c'_{C-C}$, is given by

$$d_1 = 2c'_{s-c}\cos\frac{\theta_{\angle CSC}}{2} = 4.9800a_0\cos\frac{96.20^\circ}{2} = 2.23423a_0$$
 (15.134)

where $2c'_{S-C}$ is the internuclear distance between S and C. The atoms C, C, and O define 10 the base of a pyramid. Then, the pyramidal angle θ_{ZCOC} can be solved from the internuclear distances between C and C, $2c'_{C-C}$, and between C and O, $2c'_{C-O}$, using the law of cosines (Eq. (15.106)):

$$\theta_{\angle CCC} = \cos^{-1} \left(\frac{\left(2c'_{C-O}\right)^2 + \left(2c'_{C-O}\right)^2 - \left(2c'_{C-O}\right)^2}{2\left(2c'_{C-O}\right)\left(2c'_{C-O}\right)} \right)$$

$$= \cos^{-1} \left(\frac{\left(4.95984\right)^2 + \left(4.95984\right)^2 - \left(4.9800\right)^2}{2\left(4.95984\right)\left(4.95984\right)} \right)$$

$$= 60.27^{\circ}$$
(15.135)

Then, the distance d_2 along the bisector of θ_{ZCOC} from O to the internuclear-distance line $2c'_{C-C}$, is given by

$$d_2 = 2c'_{C-O}\cos\frac{\theta_{ZCOC}}{2} = 4.95984a_0\cos\frac{60.27^{\circ}}{2} = 4.28952a_0$$
 (15.136)

The lengths d_1 , d_2 , and $2c'_{S=O}$ define a triangle wherein the angle between d_1 and the internuclear distance between O and S, $2c'_{S=O}$, is the dihedral angle $\theta_{ZS=O/CSC}$ that can be solved using the law of cosines (Eq. (15.108)):

$$\theta_{ZS=O/CR} = \cos^{-1} \left(\frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})} \right)$$

$$= \cos^{-1} \left(\frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)} \right)$$

$$= 115.74^{\circ}$$
(15.137)

The experimental [1] dihedral angle $\theta_{\rm ZS=O/CSC}$ is

$$\theta_{\angle S=O/CSC} = 115.5^{\circ}$$

(15.138)

SULFITES $(C_n H_{2n+2} (SO_3)_m, n = 2,3,4,5...\infty)$

The alkyl sulfites, $C_nH_{2n+2}(SO_3)_m$, comprise a C-O-SO-O-C moiety that comprises two types C-O functional groups, one for methyl and one for alkyl, and O-S and SO functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The SO functional group is equivalent to that of sulfoxides with $E_T(atom-atom,msp^3.AO)=0$ as given in the Sulfoxides section. The methyl and alkyl C-O 15 functional groups having $E_T(atom-atom,msp^3.AO)=-1.44915 eV$ and $E_T(atom-atom,msp^3.AO)=-1.65376 eV$, respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The SO functional group comprises a double bond between the S atom and the two unpaired electrons of O. The S atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the O-S groups is between the sulfur atom and a O2p AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy $E_{Coulomb}(S,3sp^3)$ of the outer electron of the S3sp³ shell given by Eq. (15.120) with $r_{3sp^3} = 1.17585a_0$ (Eq. (15.119)) is $-11.57099 \ eV$. Using Eq. (15.16) with the radius of the

sulfur atom $r_{16} = 1.32010a_0$ given by Eq. (10.341), the energy $E(S3sp^3)$ of the outer electron of the $S3sp^3$ shell given by the sum of $E_{Coulomb}(S3sp^3)$ and E(magnetic) is $E(S3sp^3) = -11.52126 \ eV$ (Eq. (15.130)).

Thus, the O-S group is solved as an energy minimum by hybridizing the four S3p 5 electrons to form a $S3sp^3$ shell, and the sharing of electrons between the O2p AO and the $S3sp^3$ HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus, c_1 and c_2 are equal to one in Eq. (15.52), and the energy matching condition is determined by the C_2 10 parameter. Each $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), and the S HO has an energy of $E(S3sp^3) = -11.52126 \, eV$. To meet the equipotential condition of the union of the O-S H_2 -type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a $C2sp^3$ HO, the hybridization factor C_2 of Eq. (15.52) for the O-S-bond MO given by Eqs. 15 (15.68) and (15.70) is

$$C_{2}(S3sp^{3} \text{ to } O \text{ to } C2sp^{3}HO) = \frac{E(S,3sp^{3})}{E(O,2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771)$$

$$= 0.77641$$
(15.139)

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the O-S-bond MO is the sum of the component energies of the H_2 -type ellipsoidal MO given in 20 Eq. (15.42) with E(AO/HO) = 0 and $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$. For sulfites, $\Delta E_{H_2MO}(AO/HO) = -0.92918 \, eV$ and equivalently, $E_T(atom-atom,msp^3.AO) = -0.92918 \, eV$ (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 15.175 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Functional Group	Group Symbol
C-O (methyl)	C-O (i)
C-O (alkyl)	C-O (ii)
O-SO ₂	O-S
SO	SO
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H\left(CH_{2}\right)$
СН	C – H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

		_	т	-	_					_	1		,
	(J) 2-2	g 5	2 1070	2,101,25	1.45164	1.53635		1.532	(propane) 1.531	(buttone)		1.52750	
	(3) 2-2	dines	2 10735	4.1012	1.45164	1,53635		1.532	(propane)	(butane)		1.52750	
	C-C (d)	don	2 12499		1,43744	1.54280		1.532	(propage)	(butane)	31773	010401	20000
	C - C (e)		2,10725		1.45164	1.53635		1,532	(propane)	(buttane)	1 57750	Ve126.1	00000
	(4) 2-2		2.12499	1 45744	14.7 Ch.1	1.54280		1.532	(propane) 1.531	(butane)	1 54616	2	COYBY
	C-C (a) Group		2.12499	1 45744		1.54280		1.532	1.53	(ontano)	1.54616		- XXX
l	C-H Group	l	1.67465	1.05661		1.11827		211	(isobutane)		1.29924	10000	20000
	C-H (CH ₂)	Group	1.67122	1.05553		1.11713		1.107 (C-H propane)	1117	(C. I. Duranic)	1.29569	0.62160	10000
	C-H (CH,)	1	1.64920	. 1.04856		1.10974		1.107 (C - H propane)	1.117 (C-H butane)	,	1.27295	DARKEN	
5	50		1,96517	1,40896		1,49118		1.485	(ametiny) sulfoxide)		1.9847	0.70974	
٥	7	00001	1.10237	1,48102		1.36744		1.574	(H ₃ ,SO ₄)	0,000	0.64009	0.86966	
(J-0-1)	Group	1.7047		1.33968		1.41785				0,10470	67461.1	0.74645	
0-0-0	Group	712021		1,34431		1.42276			-	ALTOL I		0.74388	
Parameter		a (a.)		c' (a,)	Dond	ير. (ع)	Evp.	Bond	Ē	b.c (a)	(ű	

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Table 15.179. The MO to HO intercept geometrical band parameters of alkyl sulfites. R. R. R. are H or alkyl groups.	netrical bon	d parameters of	alkyl suifites. A	K, K', K' are H o		5	1 - anni, nisp .AU	10							
	Atom	18,	난	12	, i	Final Total	1	Í	F. Control	$E(C2sp^2)$	60	6	6	o	o"
	-,	Seg.	. (cV)	(eV)	(eV) Bond 4	7 (Page 18)	(°	(°°	Final	ટું	©	<u> </u>	೯	(a)	(a)
	_			a ahaa		(eV)		_		a l					
	S	0	0.46459	-0.464S9	0		1,52010	0.86359	15.75493		78.56	101.44	37.25	1,58026	0.17130
	0	0	0	0	0		000001	17710.0	14.82575		90°H	95,54	40.75	1.50400	0.09304
ľ	٠.:	0.46439	0.46459	0	0		1,32010	0.86339	-15.75493		126.68	z:cs	55.47	12530.0	0.51581
	0,	45 my 0-	. 12457	0	D		000001	0.84957	-16,01492		126.03	53.57	54.81	0.98133	0,49969
	0	-0.4FH39	-0.82688	0	. 0		00000'1	0.24418	-16.11722		125.77	54.23	\$£.56	0.98753	0.49349
	0	-0.72457	-0.46459	0	0		1.00000	0.24957	-16.01492		93.85	16.15	44.57	15786.1	0.05700
	ن	.0.72457	e	c	¢	-132.34026	0.91771	0.87495	-15,53033	-15.35946	95.98	14.02	46.10	91825.1	0.09112
	0	-0,NZ6NB	40,46459	С	c		1,00000	0.84418	-16.11722		94.50	15.50	44.80	1,27343	0.06624
	ڻ	-0 8268R	81626'0-	0	0	5717E.E21.	17716.0	0.12053	-16,58181	-16.39093	92.41	17.59	43.35	1.30512	0.03456
	i	#16Z6.0-	e	o		152.54487	0.91771	0.86339	-13.75493	-15,56407	77.49	102,51	41.48	1,23564	0,18708
	L	#1626.0-	-0.9291K	•		-133,47406	17716.0	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	135416	0.29933
	i	#1626.0- ·	0.92918	0.92918	0	-154,40324	0,91771	0.77247	-17,61330	-17,42244	61.10	118.30	31.37	1,42988	0.37326
ŀ	ن	-0.92918		C C	0	152.54487	0,91771	0.16359	-15,75493	-15.56407	rg.83	116,18	30,08	1,43879	0.38106
	ď	1 -D.92918	अध्यत्यः ०-	а	0	-153.47406	17710.0	0.81549	-16,61412	-14.49325	36.41	123.59	20.06	1.90320	Q45117
	ئ	#JOZOT:	-0,9291R	#1626 U*	6	-134,40324	17716.0	0.77247	-17,61330	-17.42244	48,30	02.181	21.90	1,97162	0.51388
$h - H_2C_2(R^2 - H_2C_2)C_3(R^2 - H_2C_3)C'H_2 - C(C)$	ť	-0.9291K	-0.72457	-0,72457 .	-0.72457	-154,71860	17710.0	0.75RK9	-17.92866	-17.73779	48.21	131.79	21.74	H256.1	0.50370
		-0.92918	-0.92918	D.92918		-154,40324	0.91771	0.77247	-17,61330	-17,42244	48.30	131.70	21.90	1,97162	0.51388
(C-C'(B))	ڻ	40.72457	1224.57	. 40,72457 -	-0.72457	-154.51399	17716.0	0.76763	-17,92866	QTT&T,TI-	50.04	129.96	. 3972	1.94462	0,49298
	٠	2517.2 0-	н1626.0-	-0.9291#	ů.	-154.19863	17710.0	0.78155	-17.40869	-17.21783	52.78	127.23	24.04	1,92443	0.47279
110C. (N-H.C.)C. (N-H.C.)CH	ن	0.72457	151510-	-0,72457	72427.0-	-134.51399	17716,0	0,76765	-17,92866	-17.73770	30.D4	129.96	22.66	1.04462	0.49298

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Parameters	S 0-0	(E) 0-10	8-0	8	Ť,	€,	* E	Gmus Gmus	(e)	Crown Group	(a) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	C (e)	Graup Cagno
	Canb	Cronb	droas	dnos	Group	Group	district in the second						
7	_	_	_	2		2	-	1.	-	-	-	-	-
E.	0	o	0	0	2	-	0	.0	0	0	0	0	0
n,	0	•	°	0	0	o	0	0	0	0	0	. 0	0
, i	0.5	20	0.5	0.5	0.75	0.75	0.75	0.5	0.5	5.0	6.5	0.5	0.5
ن	-	-	0.77641	-	-	-	1	1	-	-		1	1
٠,	-	-	-	_	-	_	1	-	ı	-	-	1	-
5	0.85395	0.85395	_	1.20632	0,91771	17719.0	17416.0	0.91771	17716.0	0.91771	0.91771	17716.0	17716.0
٠,	0	0	0	0	0	-	-	0	0	0	1	1	0
5	2	7	7	4	-	-	1	2	7	2	2	7	_ 2
3	0	٥	0		3	2	-	0	0	٥	0	0.	0
	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	5.0	0.5
	-	-	0.77641	-	-	1	-	1	1	-	1	1	
7, (27)	-33.15757	-33.47304	-48.93512	-82,63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29.10112
7, (2,7)	10,12103	10.15605	08981.6	19.31325	38,92728	25.78002	12.87680	9.33352	533352	9.37273	9.33352	9,37273	9.37273
T (eV)	9.17389	9.32537	14,36741	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	6,50500	6.77464	6.90500	6.90500
V. (uV)	4.58695	-4.66268	-7.18371	-10,40592	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.n m) (cV)	-14,63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15,56407	-15,56407	-15,35946	-15,56407	-15,35946	-15.35946
46 m (w) (eV)	-1,44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0 .	0	0	0
E, [so so] (cV)	-13.18574	-12.98113	0.92918	-1036001	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E, (n, no) (cV)	-31,63533	-31.63544	-31.63543	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31.63535
Er (atunt - atom, night, AD) (eV)	-1,44915	-1.65376	-0,92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
E, (sa) (eV)	-33,08452	-33.28912	-32,56455	-63.27074	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
a (1011 rad/s)	22.0240	12.1583	33.4164	17.6752	24.9286	24.2751	24.1739	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (aV)	14,49660	8,00277	21.99527	11.63476	16.40846	15.97831	15.91299	6,21159	651179	10.19220	6.21159	6.29021	6.29021
E. (eV)	-0.24921	-0.18631	-0,30214	-0.21348	-0.25352	-025017	-0.24966	-0.16515	\$1591'0-	-0.20896	-0.16515	-0.16416	-0.16416
E cm (cV)	0.13663	0.13663	0.08679	0.12832	0.35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944	0.12512 [2]	21521.0 [2]	0.12312 (2)
E (eV)	-0.18089	-0.11799	-0.25875	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10339	-0.10260	-0.10260
E_ (cV)	0,14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803
$E_r(a_{m\varphi})$ (cV)	-33,26541	-53.40711	-32,82330	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33,18712	-33.18712
E (4 m) (eV)	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489
Enter la . 10 110] (eV)	0	0	0	-1.16125	13,59844	-13.59844	-13.59844	0	0	0	0	٥	0
E. (thus) (aV)	3.99563	4,13733	3.55352	3.86856	12,49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3,91734

Table 13.181. The total bond exergics of alkyl sulfres carecutated using the functional group composition and the energies of Table 13.180 compared to the experimental values [3].

Formula Name C=O (i) C=O (ii) O=S SO C.H, C.H, C.H, C.C (a) C=C (b) C=C (d) C=C (d) C=C (f)

Group Group Group Group Group

	B. θ	C	:				107	(propane)	(propane) (propane) (butane)	(isobutano)	111.0 (butane)	(isobulane)				110.8	(aurinos)		111.4	(Isobuland)	(Geophysia)
	Cal. 9	Ξ		59 80	103.35	1	77 82	100.44	110.49		110,49		109.50	100.44	109.44	110.67	110.76		111.27		7
	9	" ©	?															1			
	9	•	:									T									
	6	· =	:			1	\perp		15.69		15.69			70.56	70.56			Ī			
, 40).	Ę	. §.		37552.1.	-1.63376	-0.72457	0						c			-1.65836			٥	-(.85836	
– atom, msp	٧.			Q. RAK3S	0.84418	0 12000	1.15796						1.157%			0,81549	LOURRY		1,04847	1.04887	
is E _r (aiom	5			-	-	-	0.73						6.75			1	4.73		0,75	0.75	1
used. Er	ئي			-	_	0.77641 (Eq.	(13.139)			1].	-			-	-		-	-	
g angle wer	ئ			-	-	-	-				-		-				67.0		5.0	0.75	
m the preceding	ڻ'	Aben 3		0,8441R	0,84418	0.77641	-				_,		-			0.81549	0,91771		1216.0	17716.0	
arameters fro	ď.	<u>*</u>		0.85252	0,84418	0.16359	OREUR D					0 87740	erow's			0.81549	D.R7493		0.87495	0.87495	
Assertable to the parameters of any sources and experimental values [1]. In the calculation of θ , the parameters from the proceeding angle were used. E_1 is E_2 (atom – atom, may AO)	Atom 2 Hybridizzion	Designation	(Table 13.3.A)	=	=	и	+					=	:			Ŋ	_		-	-	
. In the calci	Ermin	C Maria		.16,11722	271181.	10.36.01	=					=				-16.68412 C.	-H.82373	-14,82575	٠,	-14.8233	
mental values [1]	Atom I ft, bridization	Ocsignation	(Table 15.3.A)	· >	=		,					,				R	••		∽	3	
es and exper	1			2,0	-16.17 <u>12</u>	-15.75493	-15,75493					-15.75493			27.68413	-10,04412 C.	-15.55033 C,	-15,55033	مي	-15.55033	
arky: Sulli	Termina	Alres (Q _D)		74.90T	9ZH9"	91487	3,4252	L				3,423				4.795R	4, 1633		4.1633	1562.4	
and mercial of	75. Image	(°		2.96203	2.96203	2,96203	211106					1.00711	L			2.91547	2.11323		2,1577.1	72806.1	
1	7 7	(°)		2.11772	2,06205	2.68KG2	2,11106					11760.5				2.91547	2,91547	27704	4.91347	2.90327	
Ahmyd Amek				'05'07	, CO ₂ , SO ₂	\$'0.37	Methilese ZHC, H		ָ דניניני		H1.5°.37	Math.	70.07	H.J.37	77		H.J.)7	H, 3, 37	, pa	70°L	לנ"נ"

SULFATES $(C_n H_{2n+2}(SO_4)_m, n=2,3,4,5...\infty)$

The alkyl sulfates, $C_nH_{2n+2}(SO_4)_m$, comprise a $C-O-SO_2-O-C$ moiety that comprises two types C-O functional groups, one for methyl and one for alkyl, and O-S and SO_2 functional groups. The alkyl portion of the alkyl sulfate may comprise at least two 5 terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl C-O functional groups having $E_T(atom-atom,msp^3.AO)=-1.44915\ eV$ and $E_T(atom-atom,msp^3.AO)=-1.65376\ eV$, 15 respectively, are equivalent to the corresponding groups given in the Sulfites section. The O-S functional group having $E_T(atom-atom,msp^3.AO)=-0.92918\ eV$ is equivalent to that given in the Sulfites section. The SO_2 functional group is equivalent to that of sulfones with $E_T(atom-atom,msp^3.AO)=0$ as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each $E_D(comp)$ of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

A second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of t

	(J-C)	Group	.	2.10725		1.45164	35951	200		(propage)	1.53.1	(butane)		1.52750
	(e) 2-2	Group		2.10725	,,,,,,	1.45104	\$2965 1		163	(propane)	1.531	(butane)	. 63-63	1.36/30
	(p) 2-2	Cronb		2.12499	1 45744	Add Chin	1.54280		1.532	(propane)	1.531	(butane)	1 54616	201511
	(e) 2-2	die 5		2.10725	1.45164		1.53635		1.532	(propane)	1.53	(butane)	1.52750	
	(a) U-U		00/61 6	4.12.33	145744		1.54280		1.532	(propane)	2 2	(commo)	1,54616	20,00
	C-C (a)		2.12400	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	1.45744		1.54280		1.532	(propane)	(Autona)	(Aumana)	1.54616	00000
	Group	l	1.67465		1.05661		1.11827			(isohutane)		L	1,29924	300290
	$C-H(CH_2)$	Gran	1.67122		1.05555		1,11713		1.107	(n propane)	(C-H butane)	1 3000	K9CK7''	0.63159
100/11	$(H_1)H_2$	dinorio	1.64920	1.07057	1,040,0	,	1.10974		1.107	1.117	(C-H butane)	1 22208		0.63580
205				1,85851			1,44282		1.435	(dimethy)		1.26315		0.75353
0-S		00000	1.70299	48102			. 1.56744		1.574		0.84069	0.84069		
(E) 0-3	Group	54,04	21.	1.33968			1.41783					1.19429	0 74546	0. /417.2
ر-رد د-رد	Group	1.80717		1.34431		-	1.42276					1.20776	0 74388	
Biginary.		0 (0')		(0)	Bond	Length	zc. (A)	å	Bond			h,c (a,)	.,	

Table 15.184. The geometrical bond parameters of alkyl sulfates and experimental values (I

Dona	Atom	£.		£,	, ,	Final Loral		1	100	$E(C2sp^3)$	60	9	φ,	7	Ġ,
		(cV)	(eV)	(Sev)	(eV)	Care	(°)	(a°)	Final (§.	€	€	ေ	(a)	(°)
		1	3 000			(e,				Final					_
(RO), (O, X = O.	8	0	. 0	-0.46439	-0,46459		1,32010	0,86359	-15.73493		97.06	19.54	43.13	1,35635	0.00693
$(RO)_{2}(O_{n})S = O_{n}$	o,	o	٥	0	. 0		1.00000.	17716.0	-14.82575		95.05	84.95	46.36	1.28256	0.08071
CH,O S(O.)OR	S	-0.46459	-0.46459	o .	0		1,32010	0,86359	-15.75493		126.68	53.32	55.47	0.96521	0.51581
$CH_{,O_{a}} - S(O_{a})OR$	°o	-0.46459	-0.72457	0	0		1.00000	0.84957	-16.01492		126.03	53.97	54.81	0.98133	0.49969
$RCH_2O_a - S(O_2)OR'$ (C-O'(i))	oʻ	-0,46459	-0.82688		•		1.00000	0.84418	-16.11722		125.77	54.23	\$4.56	0.98753	0.49349
$H_1C_2 - O_2S(O_2)OR$ (C - O (i))	<i>"</i> 0	-0.72457	-0.46459	. 0.	0	,	1.00000	0.84957	-16.01492		93.85	\$1.08	44,57	1,28731	0,05700
$H_sC_s - O_sS(O_s)OR$ (C - O (i))	C.	-0.72457	0	c	.0	-152.34026	17716.0	0.87495	-15,55033	-15.35946	95.98	84.02	46.10	1,25319	0.001,12
$RH_1C_2 - O_4S(O_2)OR'$ $(C-O_1(i))$	0	-0 \$2688	-0.46459	0	0.		1.00000	0,84418	-16,11722		94.50	15. 50	44,80	1.27343	0.06624
$RH_1C_4 - O_4S(O_2)OR$ $(C - O_1(i))$	"	-0.82688	-0.92918	0		2717E881.	17710.0	0,82053	-16,58181	-16.19095	9241	87.59	43.35	1,30512	0.03456
C-H (CH,)	ij	-0.92918	0	ō	0	152.54487	17716.0	0.86359	-15,75493	-13.56407	77.49	102.51	41.48	1.23564	0.18708
$C - H\left(CH_{z}\right)$	Ü	-0.92918	-0.9291€	0	0	153,47406	17719.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1,35486	0.29933
C-H (CH)	υ	-0.92918	-0.93918	-0.93918	0	154.40324	17716.0	0.77247	17.61330	-17.42244	61.10	118,90	70.10	1.42988	92575.0
H,C,C,H,CH, - (C'-C: (8))	ú,	93918	0	0	. 0.	-152,54487	0.91771	0.R6359	-13,75493	-15.56407	53.82	116.18	30.08	1.83879	0,38106
$H_iC_iC_iH_jCH_i - (C_i-C_i(a))$	ڻ	-0.9291B	-0.92918	0	0 .	-153,47406	17719.0	0.81549	-16.68412	-16.49325	56.41	123.59	97.97	1.93890	0.45117
$R-H_1C_2C_2(H_2C_2-R^2)HCH_1-$ (C-C'(b))	3	81626.0-	\$1675.0	-0.92918	0	154 40324	0.91771	0.77247	-17.61330	-17.42244	48.30	07.161	21.90	1.97162	0.51388
$R = H_2C_*(R - H_2C_*)C_*(R^2 - H_2C_*)CH_2 - (C - C_1(e))$	ڻ	81626.0-	-0.72457	-0.72457	-0.72457	154.71860	0,91771	0.75889	-17.92866	67.77.71-	48.21	62.181	21.74	1.95734	0.505.0
$isoC_{\mu}C_{\mu}(H_{\mu}C_{\mu}^{\mu}-R^{\mu})HCH_{\mu}-(C^{\mu}-C^{\mu}(d))$	ີ :	-0.92918	.0.92918	81626.0-	0	+154.40324	0.91771	0.77247	-17.61330	-17.42244	48.30	02.161	21.90	1.97162	0.51388
$terK_{s}(R'-H_{s}C_{s})C_{s}(R''-H_{s}C_{s})CH_{s}-$ $(C-C'(e))$.	-0.72457	-0.72457	-0.72457	.0.72457 _.	-134.51399	17716.0	0.76765	-17.92866	-17,73779	\$0.04	129.96	971	1.94462	0.49298
$tenC_{\mathcal{C}_{i}}(H_{\mathcal{L}_{i}} - R)HCH_{2} - (C - C \cdot 0)$	ن	-0.72457	-0,92918	-0.92918	. 0.	-134,19\$63	17719.0	0,78155	-17.40869	נמרוב, רו-	52.78	27.11	24.04	1.92443	0.47279
$hsc'_{*}(R-H_{1}C_{*})C_{*}(R^{*}-H_{2}C_{*})CH_{1}-$ $(C-C^{*}(\Omega))$	ئ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51309	0.91771	0.76765	-17.92866	977.71-	20.04	129.96	22.66	1.94462	0.49298

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates. R,R',R'' are H or alkyl groups. E_{r} is E_{r} (atom-atom,msp',AO).

Parameters C = O (i) I	C-O (ii) Group 1 0 0 0 0 0 0 0 2 2 2 0 0 0 0 0 0 1 1 1 1	0 0 0 0 0 0 0 0 0 0.77641 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	SO, Group 0 0 0 0 0 1 1 1 1 1,20632 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Group 3 2 2 0 0 0 1 1 0.91771 0.91771 1 1 1 1 1 1 1 1 1 1 1 1 1	C.P.1 Group. 2 1 1 1 1 1 1 1 1 1 1 1 1 1	Group 1 0 0 0 0 0 1 1 1 1 1 1 1	Grup (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Cruck) (Group 1 0 0 0 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1	Graup Graup 0	Group Group 0 0	Group 1 0	Group 0 0 0
(4)	0 0 0 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.	0 0 0 0.77641 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.75 0.91 0.91773 0.91773 0.75 0.75 0.75 0.107.32728	1 0 0 0 0.75 0.091771 0.091771 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0.5 11 1 0.5 1711	0 0 0.5	- 0 0	0 0	0 0	0 0 0
	0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0.5 0.77641 1 1 0 0 0.5 0.7641 -48.03512 9.18680	0 0 0.5 1 1 1 1 1 1 20632 1 0.5 0.5 1 9.92103	3 2 0 0 0 1 1 1 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1	2 0 0 0.75 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 0 0 0 0 0.75 0.75 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 0 0,5 1 1 1 0,51,711: 0,01,711:	0 0 0	- 0 0	- 0 0	00.	- 0 0 5
	0 0 0 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.	0 0 0 0 0.5 0.5 0.7041 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0.5 1 1 1 1 1 1 1 1 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	2 0 0 0.75 1 1 0.91771 0 1 3 0.75 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 0.75	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0.5 1 1 1 0.91771	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0	0 0	0 0	0 0 0
	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0.5 1 1 1 1,20632 1 1 8 8 8 1 1 0.5 	0.75 0.75 1 1 0.91771 0 1 3 0.75 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0 0.75 1 1 1 0.91771 1 2 2 0.75	0 0.75	0 0.5 1 1 0.9(77)	0.5	0	0	0.	0 0
	0.5 1 1 0.85395 0 0 0 0 0 0 0 1 1 -33.43304 10.15605 9.3258	0.37641 1 1 0 0 0 0 2 2 0 0 0 5 0.35 0.77641 -48.03512 9.18680	0.5 1 1 1.20632 1 1 8 8 1 1 0.5 	0.75 1 0.91771 0 1 3 0.75 1 1 1 1 1 1 1 1 1 1 1 1 1	0.75	0.75	0.5	0,5		0.0		0.5
	1 0.85395 0 0 0 0 0 0 0.5 1 1 33.4304 10.15605 9.3258	0.77641 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0	1 1,20632 1 8 8 1 1 1 1 1 1 1 180,36434 39,92103	0.91771 0.091771 1 3 0.75 1 1 1 1 1 1 1 13.92728	0.91771	1 0.91771	1 1 0.91771: 0	-	0.5	;	0.5	}
	0.85395 0 0 2 2 2 0 0 0.55 1 1 33.4304 10.15605 9.3255	1 1 0 0 0 0 0 0 0 0.5 0.77641 -48,03512 9,18680	1 1,20632 1 8 8 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0.94,771 0 1 1 2 0,75 0,75 1 1-107,32728	0.91771 1 1 2 2 0.75 1	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 0.91771: 0		-	-		-
	0.85395 0 0 0 0 0 0 0.5 1 1 -33.4304 10.15605 9.3258	0 0 0 0.5 0.77641 -48,03512 9,18680	1,20632 1 8 8 1 1 0,5 1 180,36454 39,92103	0.94771 0 1 3 0.75 1 1 -107.32728	0.91771 1 1 1 2 2 0.75 1 1	1 1 1 0.07.71	0.91771	-	-	-		-
	0 2 0 0 0.5 1 .1 -33.47304 10.15605 9.32537 4.66268	0 2 0 0.5 0.77641 -48,03512 9,18680	8 8 1 0.5 1 -180,36454 39,92103	0 1 3 0.75 1 1 -107.32728 38.92728	1 1 2 2 0.75 1	1 1 0.75	2	12216.0	0.91771	0.91771	17716.0	17716.0
	2 0 0.5 1 -3.47304 10.15605 9.32337 4.66268	2 0 0 0.5 0.77641 -48.03512 9.18680	8 1 0.5 1 -180,36454 39,92103	1 3 0.75 1 107.32728	0.75	1 0.75	2	0	0	-	_	0
	0 0.5 1 -33.47304 10.15605 9.32337 4.66268	0 0.5 0.77641 -48,93512 9.18680 14,36741	. 0.5 1 1 -180,36454 39,92103	3 0.75 1 1-107.32728 38.92728	0.75	1.0		2	2	2	2	2
	0.5 1 -33.47304 10.15605 9.32337 -4.66268	0.5 0.77641 -48,91512 9.18680 14,36741	0.5 1 -180.36454 39.92103	0.75 1 -107.32728 38.92728	0.75	27.0	0	. 0	0	0	0	u
	1 -33.47304 10.15605 9.3237 -4.66268	0.77641 -48.93512 9.18680 14.36741	1 -180,36454 39,92103	1 -107.32728 38.92728	-70,4) 425	-	0.5	5.0	2.0	0.5	0.5	0.5
	-33.47304 10.15605 9.32537 -4.66268	-48,93512 9.18680 14,36741	-180.36454	-107.32728 38.92728	-70.4 \ 425		-	-	-	_	-	-
	10.15605 9.32537 4.66268	9.18680	39.92103	38.92728		-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (cV) 10.12103	9.32537	14.36741			25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9,37273
T (eV) 9.17389	4.66268		48.52397	32.53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (uV) 4.58695		.7.18371	-24.26198	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(+0 10) (eV) -14.63489	-14.63489	0	-11.52126	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$\Delta E_{n_1,n_2}(n m) (cV)$ -1.44915	-1.65376	-0.92918	-1.16125	0	0	. 0	0	. 0	0	0	0	0
Er (no m) (eV) -13.18574	-12,98113	0.92918	-10,35001	-15,56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
. (E, (n, m) (c/)	-31,63544	-31.63543	-126.54154	-67.69451.	-49.66493	-31,63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	-31.63535
Er (alon - alon, msp3. AO) (eV) -1.44915	-1,65376	-0.92918	0		0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
Fr (1m) (aV) -33.08452	-33,28912	-32.56455	-126.54147	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
a (10 ¹⁵ rad / s) 22.0240	12.1583	33,4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (cV) 14.49660	8.00277	21.99527	7.59437	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6,21159	120679	120679
	-0.18631	-0.30214	-0.17247	-0.25352	-0.25017-	-0.24966	-0.16515	-0.16515	-0.20896	51591.0-	-0.16416	-0.16416
$\overline{E}_{\text{kin}}(aV)$ 0.13663	0.13663	0.08679	0.12832	0.35532 (Eq. (13.458))	0.35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978	0.09944	0.12312	21521.0	0.12312 [2]
Υ	-0.11799	-0.25875	_	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
11, (eV) 0.14803	0.14803	0,11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Kr (5-4) (eV) -33.26541	-33.40711	-32.82330	-126,97472	- 67.92207	-49.80996.	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
E, (v. 10'10) (eV) -14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Emmo (s, so mil (cV) 0	0	0	-1.16125	-13,59844	-13.59844	-13.59844	0	0	0	0	0	0
En(com) (eV) 3.99563	4.13733	3,55352	8.61994	12.49186	7.83016	3.32601	4,32754	4.29921	3.97398	4.17951	3.62128	3.91734

(a) C-C(b) C-C(f) Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

Formula Name C - O (i) C - O (ii) O - S SO_s CH_s CH_s CH_s CH_s C - C (a) C - C (b) C - C (d)

Group Group Group

	Exp. 0		120.9 [44] (dimethyl culfule)	109.67 [44] (dimethyl sulfare)	103.85 (44) (dimethyl sulfate)	i 17.43[44] (dimethyl sulfate)	107 (propene)	112 (propana) 13.8 (butezro) 110.8 (robatane)	111.0 (butane) 113.4 (isobutane)				1 to 8 (isobutane)		111.4 (isobutane)	111.4 (isobutane)	
	Cal. θ	<u> </u>	120.44	110.26	103.35	117.84	108.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.22	72.111	107.50
ļ	°, €	2														-	
İ	6 G	C															
	(ه)	5						15.93	69.51	•	70.56	78.55					25.50
40).	E,	.	-1.65376	37883.1-	-1.65376	-0.72457	6			0			-1.85836	o	0	-1.85836	
-atom, msp	5		0.85252	0.84815	0.844/8	0.82000	1.15796			1.15796			0.81549	1.04887	1.04887	1.04887	
is $E_{r}(arom$	ئ		-	_	_	-	0.75	·		0.75			-	67.9	0,75	0.75	
e used. Br	5		-	-	-	0.77641 (Eq. (15.139))		1		-			-	-	-	-	
g angle wer	ئ			-	-	_	-			-			-	0.73	0.75	0.75	
the precedin	5 Alvai		0.85252	0.84418	0.84418	0,77641 (Eq. (15.139))	-			_'			0.81549	17716.0	14416.0	0.91771	
rameters from	C ₂		0,85252	0.65252	0,84418	0.86359	0.86359			0.86359			0.81549	0.87495	0.87495	0,87495	
lation of θ , , the pa	Atom 2 Hybridization	Table 15.3.A)	٠.	=	=	s	Н		,	x			52	-	-	,	
In the calcu	F. inhaha		-15.95954	-16.11722	-16.11723 O,	1003£.01-	ж		·	r			-16.68412 C.	-14.82575 C.	-14.82575 (?	-14.82575 C.	·
mental values [1].	Atom		0	o	~	,	7						25	\$	٤	۶	
and experi	A Park		,15,95954 ()	115,95954	.16.11722	-15 75493	-15.75493	•		-15.75493			-16.68412	.15.55031	-15.55033 C.	-13.55033 C ₁	
alkyl sulfate		Abims (a,)	4.7339	4.66%	4,6476	4 8416	3.4252			3.4252			4,7958	4,1633	4,1633	4,7958	
rameters of	2c.	(a,)	2,72654	1.96203	1,96203	2,96203	2.11106			2.09711			2.91547	2.11323	2.09711	2,90327	
ոժ angle pa	2c' ihad 1	(a')	2,72654	2,72654	1,96203	2.68862	2.11106			209711			2,91547	2.91547	2.91547	2.90327	
Table 15.188. The bond angle parameters of alkyl sulfates and experimental values [1]. In the calculation of θ_c , the parameters from the preceding single were used. E_f is E_f (atom — atom, map? AO)	Alman of Argh		'08'07	°08"07	'os'oz	s'o".)7	Methology ZHC,H	':5':5':57	н'5'.	Medel .	'J'J'J7	H1.5.37	") wi ")",)";)/?	70°C, H, 2,72	LC,C,H	בכיכי כי ומו כי	7C,C,C,

NITROALKANES
$$(C_n H_{2n+2-m} (NO_2)_m, n=1,2,3,4,5...\infty)$$

The nitroalkanes, $C_n H_{2n+2-m}(NO_2)_m$, comprise a NO_2 functional group and a C-N functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state ${}^4S_{3/2}^0$. The bonding in the nitro (NO_2) functional group is similar to that in the SO_2 group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO_2 group, the two unpaired electrons of the O atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the 20 nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the $C2sp^3$ HO. In nitroalkanes, the $C2sp^3$ HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)), the N AO has an energy of $E(N) = -14.53414 \, eV$, and the O AO has an energy of $E(O) = -13.61806 \, eV$ [38]. To meet the equipotential condition of the union of the N = O bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771)$$

$$= 0.85987$$
(15.140)

Since there are two O atoms in a linear combination that comprises the bonding of the NO_2 group, the unpaired electrons of each O cancel each others effect such that E_{mag} is not subtracted from the total energy of NO_2 . Additionally, $E_T(atom-atom, msp^3.AO) = -3.71673 \, eV = 4(-0.92918 \, eV)$ (Eq. (14.513)) is the maximum given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The C-N group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and $\Delta E_{H_2MO}(AO/HO) = -0.72457 \ eV$ for nitroalkane and $\Delta E_{H_2MO}(AO/HO) = -1.44915 \ eV$ for primary amines. Whereas, $E_T(atom-atom,msp^3.AO) = -1.44915 \ eV$ for both functional groups. This condition matches the energy of the C-N group with the NO_2 having $\Delta E_{H_2MO}(AO/HO) = 0$.

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 15 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.192 corresponding to functional-group composition of the molecule. E_{mag} given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using 20 Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Functional Group	Group Symbol
NO₂ group	NO_2
C-N	C-N
CH ₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

C-C (f) Group	2.10725	1,45164	1.53635	1.532	(propane)	1.531	(butane)	1.52750	0.68888
Group	2.10725	1,45164	1.53635	1.532	(propane)	1.531	(butane)	1.52750	0.68888
Group	2.12499	1.45744	1,54280	1.532	(bropane)	155.	(butune)	1,54616	0.68600
C - C (c) Oroup	2.10725	1.45164	1,53635	1.532	(propare)	1.531	(butane)	1.52750	0,68888
رام ن مسمل مسمل	2.12499	1.45744	1.54280	1.532	(propane)	1.53	(betane)	1.54616	0.68600
C'-C (a) Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1.54616	0.68600
C - H Group	1.67465	1,05661	1.11827		71.12	(isobutane)		1.29924	0.63095
('-H (CH ₁)	1.67122	1.05553	1,11713	1,107	e) (C - H propane)	1.17	(C - H butane)	1,29569	0.63159
C-H (CH.) Group	1.64920	1.04856	1,10974	1.107	6	1.117	ĕ	1,37295	0.63580
C-N Group	1.97794	1.40639	1.48846		1.489	(nitromethane)		1.39079	0.71104
<i>NO</i> ; Group	133221	1.15421	1,22157		22.	(nitro:nethane)		0.66526	0.86639
Parameter	0 (a,)	c. (a)	Bond Length 2c' (A)	Fyn Bond	Leneth		<u> </u>	A.C. (O.)	o .

0,51864 0,51864 0,14484 0,27620 0,27620 0,21422 0,19734 0,37376 a, <u>a</u> 0.340x9 0.63558 1.53123 1.67259 1.62061 1.3354 1.35476 °0 '0' 66.50 38.35 38.35 31.71 31.24 31.37 36.08 21.90 3.0 ø, 🖭 44.75 48.45 99.35 110.70 105.04 107.51 111.53 111.53 30.9% ø_ 🕥 135.25 131.57 80.47 69.30 77.49 68.47 61.10 63.82 .¥.6 48,30 4X,30 48.21 80.0 52.7R 50.04 . O -16.28864 -15.56407 -16.49325 -17.42244 -15.56407 -16.49325 err.r. -1721783 E(*C.s.p.*) (eV) Final -15.75403 -17.40869 -17.40869 -17.40869 -16.47951 -16.68412 -16.68412 -17,61330 17,92866 First S 0.78155 0.78155 0.78155 0.78155 0.82562 0.81340 0,843359 0,77247 0 758NS £ (\$ 17714.0 17714.0 17716.0 17710.0 17716.0 17716.0 0.91771 17716,0 16 Final Total
Energy
C'2vp'
(eV) -153.24945 -152.54487 -153.47406 -154.40334 -152.54487 -153,47406 -154,40524 -154,41324 15451399 R.R.R. are H or alkyl groups, E, is E, -0.73457 (eV)
Bond 4 -0.72457 0.72457 (eV) Bond 3 -0.92918 -0,72457 -0.72457 -0.92918 -0.72457 Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes. -0,92918 0 -0.92918 -0.92918 £, (eV) Bond 2 -0.92918 -0.92918 -0.72457 -0 72437 0 -0,9291R -0,92918 E_T (eV)
Bond | -0.92018 41,92914 -0.72457 -0.92919 R1020.0--0.9291K 41626.0 2 2 5 Atom ان 2 0 0 0 0 ٠, <u>ن</u> ا ಚ ∵ ڻ ئ ٠,٩ RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O) = O - RN(O

Parameters MI_2 $C-N$ C_1 $Gram$ Group $Gram$	Arraina Grania	C-N Group	CH, Group	C.K.1	Group	C - C (a) Group	C-C (b)	(a) (b) (c) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	C-C (d) Group	Group Group	Grant Grant
n,	~	-	3	7	-	-	-	-	-	1	-
n,	0	0	2	-	•	0		0	0	0	0
É	٥	0	0	0	0	0	0	0	0	0	0
ŭ	0.5	0.5	0.75	0.75	0.75	6,5	50	6.0	6.5	0.5	0.5
	-	-		_	-	-	1	1	ı	1	-
6,		-	-	-	-	1	ı	7	1	1	-
	0.85987	0.91140	17710	0.91771	17716.0	17716.0	17716.0	17716.0	17716.0	17716.0	14160
-5	0	o	c	-	-	o	0	0	1	1	0
	4	2	-	-	-	2	2	2	7	7	2
,5	٥	0	3	2	1	0	0	0	0	0	0
	2.0	0.5	0.75	0.75	0.75	0.5	2,0	5,0	6.5	0.5	0.5
	-	1	-	1	1	-	-	_		-	-
V, (eV)	-106.90919	-31.36351	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
V, (eV)	25,57588	9.67426	38.92728	25.78002	12,87680	9,33352	9.33352	9.37273	-9.33352	9.37273	.9,37273
T (05)	40.12475	7.92833	32,53914	21.06673	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6,90500
7 (87)	-20.06238	-3.96416	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3,45250	-3.45250
Eln m) (eV)	٥	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15,35946	-15.35946
ΔΕ _{4,100} (.0 m) (cV)	۰	-0.72457	0	0	0	0	0	0	0	0	0
E, (so 10) (0V)	0	-13.91032	-15,56407	-15,56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E, (n,in) (aV)	-63.27093	-31.63540	-67.69431	-49.66493	-31.63533	-31.63537	-31.63537	+31.63535	-31,63537	-31.63535	-51.63535
$E_{\tau}(ann - alom, msp^*, AO) (eV)$	-3.71673	-1,44915	0	. 0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
Er (10) (0V)	-66.98746	-33.08452	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
@ (1013 rad/s)	19.0113	10.5087	24.9286	24.3751	24.1759	6,43699	9.43699	15.4846	9,43699	9,55643	9,55643
(aY)	12,51354	6.91703	16,40846	15,97831	15,91299	6,21159	6.21159	10.19220	6.21/59	6.29021	6,29021
$\vec{E}_{\mu}(vV)$	-0,23440	-0.17214	-0.25352	-0.25017	-0,24965	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ex. (aV)	0.19342	0.10539 [45]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0.12512 [2]	0.17978	0.09944	0.12312 [2]	0.12312 [2]	0,12312 [2]
E. (aV)	-0.13769	-0.11945	-0.22757	-0.14502	-0.07200	-0,10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (cV)	0,11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803
Experient (eV)	-67.26284	-33.20397	-67,92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33,18712
E (4. 10 00) (cV)	-14.63489	-14.63489	-14,63489	-14,63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emmilion no (cV)	0	0	-13,59844	-13,59844	-13,59844	0	0	0	0	0	0
Fr (nump) (aV)	8.72329	3.93419	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 13.193. The total bond energies of niroalkanes calculated using the functional group composition and the energies of Table 13.192 compared to the experimental values [3]. The magnetic energy E_{act} that is subtracted from the weighted sum of the E. (bea.) (c.f.) values based on commonition is given by (15.38)

() () () () ()	(e.v.) (e.v.) values based on composition is given by (15.56)	ilion is given by (1.	5.56).										1			
Formula	Name	COM	ک ان	ĆΉ,	ï#.	H.S	((. (a)	(a)	() - (, (c)	C-C (d)	(e) C-C	(J)	E	Calculated Total Boad	Experimental Total Bond	Reladve Error
		Group	dious							;	į			Energy (cV)	Energy (eV)	
ON HU	Naromorhano	-	-	-	-	-	•		•	6	0		o	25.14934	25,107	-0.0016R
CHINO	Nitrocthano	~	-	_		٥	-	0	0	٥	c	c	0	37.30704	37.292	-0,00040
CHINO	L-Nitropropane	-		-	7	c	7	c	•	c	c	0	0	49,46474	49,451	• 0.0002X
CHYNO	2-Nitropropono	_	-	~	0	_	٥	7	c	0	0	o	0	49.56563	209'61	0.00074
C'H'NO	1-Nitrobutane	-	_	_		٥	~	0	0	0	0	0	0	61,62244	109.19	-0.00036
CHINO	2-Nitroisobatan	-	_	•	0	0		0	-	c	0	0	7	61,90697	25 55	0,00061
CHINO	1-Nitropomane	-	_	_	7	٥	•	c	0	c	•	0	0	73,78014	73,739	-0.00028

1000	The same capean					III (NG CANCULA)	non of o', the para	meters from th	to preceding any	gle were use.	d. E. is E.	. atom - ate	OF asi						
ordery in column	,, 7,	, zc.	7¢,	3	Atora I	Ŀ	Alom 2						1200						. •
] E	(°)	Teminal Atem (0,)	5 -	Hybridization Designation	Alone 2	Hybridization Designation	s. Í	v į		ر. ان	ت. ت	ν.	£ 5	o, 3	6 3	θ ₂ Cal. θ		Esp. 6
				-+	(Table 15.3.A)		(Table (5.3.A)							<u></u>	<u> </u>		- E		2
LNC,H	2.11279	2,09711	3.9663	-14.X2575	_	-14.53414.	z	1771670	0.91140 (Eq. (13.116))	0.73	-	67.0	0.99312	•		-	ě	71 901 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	107 (nitramethane
'ON' 07	2,30843	2.30843	<u> </u>	O.	72	-16,08411	7.	0,81549	0,81349	-	-	-	0.81549	-1.44915		1			123
Mathibia ZHC_H	211106	2.11106	3.4252	.15.75493	,		Ξ	0.16359	_	-	-	1,0	, in the second				-	-	(aitremethane
			ŀ			I				-	-	2	AV.CI.1	0			5	108.±	pane)
ש"נ'נ'															15.60		2	(pad)	(propine) (Putano) (butano)
				L												_	_	- 48	10.8 Hime)
ZC,C,H															1509		=	三夏二 1049	6 <u>6</u> 7
H, JH2	207711	2.09711	3.4252	-15.75493		ı	Ŧ	O.RG359	_	-	-	6.75	1620				+	┿	otane)
ZC,C,C,										1			2				60.	05,001	
H"J"777							†			1					70.56	-	109.44	3	
ר. קניינייני	2,01547	2.91547	4.7USK	-16.68412 C	n	-16.68412	n	ORISAS	0.31549	-	-	-	3		32.5		109.44	┝╌┼╴	Ι,
H',5',57				-15.55033		24 E P P P				-	-	-	C8(34)	-1,43836			110.67		(isobotane)
, 1	291547	2.11323	4,1633	υ,	•	· ·	-	0.87493	0.91771	0.75	-	67.0	1.04137				110.76	22	
ZC,C,H In C,	2.91347	112007	4,1633	-15.55033		-14.82575 C.	-	0.87405	0.91771	67.0	-	67.0	1.04187	0		+		=	. 3
سرز" 70:27	2.90327	2,00327	4,705k	.15.58033	3	-14.82575	-	SGP4X D	0.91771	0.75	-	15	1			+			9
7C,C,C,						:								oraca.i.			111.27	(fsobutane)	- ()
										_		-							

ALKYL NITRITES $(C_n H_{2n+2-m} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$

The alkyl nitrites, $C_nH_{2n+2-m}(NO_2)_m$, comprise a RC-O-NO moiety that comprises C-O, O-N, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise 5 methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^22s^22p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The electron configuration of nitrogen is $1s^22s^22p^3$, and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state ${}^4S_{3/2}^0$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the O-N functional 20 group that is further energy matched to the $C2sp^3$ HO of the C-O functional group. To meet the equipotential condition of the union of the $N=O-H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the N=O-bond MO given by Eq. (15.140) is $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the N=O bond which requires that two times E_{mog} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally, $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H_1MO}(AO/HO)$ are equal to -0.92918~eV (Eq. (14.513)) which matches the energy of the N=O bond with the contiguous O-N bond and matches the energy contribution of an oxygen atom.

The O-N functional group comprise a single-bond, H_2 -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the C-O functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the C-O-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO\ to\ O)=0.85395$. The hybridization factor c_2 of Eq. (15.52) for a C-N-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO\ to\ N)=0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for O-N that bridges the C-O and N=O bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727$$
 (15.141)

10 $E_T(atom-atom,msp^3]AO) = -0.92918 \ eV$ in order to match the energy of the NO group and $E(AO/HO) = -15.35946 \ eV$ in order to match the C-O functional group.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that $E_r(atom-atom,msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are both -0.72457~eV which matches the energy contribution of an independent $C2sp^3$ HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15,195. The symbols of	Table 15, 195. The symbols of functional proups of alkyl nitrites.
Functional Group	Group Symbol
NO group	(M)
20	N-0
ဝှင	0-0
CH, group	$C = H (CH_3)$
CH ₁ group	C - H (CH,)
ಕ	: #::
CC poud (u-C)	(, - (, (a)
CC bond (iso-C)	(g) U = U
CC bond (ten-C)	30-0
CC (iso to iso-C)	€ U-U
CC (to t-C)	(a) () - ()
CC (t to iso-C)	S (1-1)

	2-2	+	7.10	1.451	1.536		_	Edonq)		+	1761
	(e) 2-2	, , ,	7.10/23	1.45104	1.53635		1.532	(propane)	(Amfang)	(Common)	06/76
	C-C (d)	00761.6	665777	1.42/44	1.54280		1.532	(propare)	(butane)	1 84616	I.SAUJO
	C~C (c)	2 10725	746164	101617	1.53635		1.532	(propane)	(Purfanc)	1 52750	201.45
	(a) C~C (b)	2 12490	1.45744	T. Janes	1,54280		1,532	(propane)	(butane)	154616	
	C-C (a) Group	2 12499	1 45744		1.54280		1.532	(1831	(butane)	1.54616	
	C-H Group	1.67465	1.05662		1.11827		13	(isobutane)		1.29924	
	C-H (CH ₂)	1.67122	1.05553		61711.1	1	1.107 (C - H ramana)	1.117	(C~H butane)	1.29569	25,53
nmental values [1].	C-H (CH,)	1.64920	1.04856		1,10974		(C - H propane)	1.117	(C-H butane)	56272.1	005-50
its of alkyl nitrites and experimental values (1	dnos0 O~J	1.85327	1,36135		1,44079		1.437	(methy) nitrate)		1,25751	0.73457
	O-N Group	1.76440	1.32831		1.40582	1 603	(methyl nitrate)	1,432	(HNO,)	1.16134	0.75784
able 13.1%. Induction that bond paramete	Croup Group	1.32255	1.15002		1,21713	1 206	(methyl nitrate)	7.5	(HNC),)	0.65314	0.86955
2010 12	Parameter	0 (0,)	c, (a,)	Bond	Se' (₹)		Length	· =		h.c (a,)	

Table 15, 197. The MO to HO intercept genmetrical bond parameter	netrical bon		of alkyl nitries. If, If, I'me H or alkyl groups. L., is L., alom - aloni, msp' A()	K, K, K ne H o	r alkyl groups.	Lr 13 Ly aron	n – alom, msp .,	£7.							
Bond	Atom	15.7	ſĨ,	12,4	E,	Final Total	, E	Ž	E Contract	E(C25p")	6	9	9	9	7
		(eV) Bond I	(eV) Bond 2	(eV) Band 3	(cV) Bond 4	Casp Control	(°	(%)	Final (eV)	(cV) Final	Ξ	©	Œ	(a)	(0°)
RONFO	6	-0,46439	0	•	٥		1.00000	O.NR9X3	-15 23034		137.15	42.15	05'29	0.49764	0.63238
RON = O	2	-D,46459	-0.46459	c	0		0.93084	0.86359	-15.75493		60 YE)	43.91	1 P. W. W. W.	0.52747	0.62221
RO, -NO,	ήυ	.0,46459	42550-	0	0		1,0000	0,86923	15,65263		99,22	NO.7K	47.63	1.18905	0.13925
RO, - NO,	ν	USPUTO-	-0.46459	g	С		0.93014	0.86359	-13.73493		98,78	\$1.22	47.30	1.19655	0.13175
$RH_{i}C_{s} - O_{s}NO_{s}$ $R = H_{i}alkyl$	ά,	-0.36229	45+9+0+	c	0 -		1,00000	0,86923	-15,45265		91.43	18.57	17.64	13962.1	0.02173
H,C, -0,NO.	[C.]	-0,36229	o	e		N2779,181.	0,91771	0.89582	-15.18804	14,99717	17.86	86.29	15.21	136342	0,05793
-CH,H,C, -0,NO,	ij	6TZYE'U*	×16260	0	٥	.152.90716	0.91771	0.84418	-16.11722	-15.92636	89.16	70.8H	42.16	(357	0.01238
$C-H\left(CH_{s}\right)$,	-0.92918	3	D.	0	-152 54487	0.91771	0.86359	-15 75493	15.56407	77.49	15201	11.48	13364	Q.1570X
$(C-H(CH_2))$, ,	X1620'0-	-O 0291X	0	0	153,47406	0.91771	0.81549	-16.68412	-16.49323	68.47	111.53	35.84	135416	0.29933
(H (CH)	ن	#1676'0*	-41.9291X	*1626'0*	c	-154,40324	0,91771	0.77247	-17.61330	-17,42244	61.10	118.90	31.37	1.42988	0,37326
H,C,C,H,CH2- (C,-C'(a))	(,,	#1620.0-	u	u	c	152.54487	0,91771	0,86359	-15.75493	-15,56407	63.82	116.18	30.08	1,43179	0.38106
H,C,C,H,CH2 — (C — (* (*))	رځ	#16ZG'0*	#1676 D-	· c	o	-153,47406	0,91771	0,81549	-16.64412	-16,49325	\$6,41	92.551	26.06	1.90190	0.45117
$R - H_1(',C_*(H_2C_* - R))HCH_2 - (C - C_*(b))$		#14E6'0-	-0.9291K	-0.9291ж	O	-154.40324	0.91771	0,77247	-[7,61330	-17.42344	4830	131.70	21.90	1,97162	0.513##
$(R - H_2C_s(R - H_2C_s)C_s(R^2 - H_2C_s)CH_2 - (C - C(6))$	ن	-0,92918	-0.72457	15121.0-	12457	-154.71860	0,91771	Q.75119	-17.93866	-17.73779	48.21	67.161	21.74	LETZE.1	0.50570
$kaC_{J_{s}}(H_{s}C_{s}-H^{\prime})HCH_{s}-(C^{\prime}-C^{\prime}(d))$	ני	#1676'D-	x1620'0-	к1626'0-	0	-154.40324	0.91771	0,77347	-17.61330	-17.42244	4830	131.70	21.30	1,97162	0.51388
(C-C'(0))	5.	1577.0-	-0.72457	-0.72437	-0.72457	.154.31379	17710.0	0,76765	-17.92866	617.771-	50.04	967723	9972	1,94462	0.4929%
$norC_{\mathcal{L}}(H_{3}C_{s}-R)HCH_{3}-(C-C, \emptyset)$	۲,	-0.72457	#16 2 2.0-	#10 <u>2</u> 0.0-	ų	-154.19863	17710.0	0,78155	-17,40169	-17.21783	52.78	22.721	74,04	1,97443	0.47279
$kaC_{\mu}(R-H_{\mu}C_{\mu})C_{\mu}(R-H_{\mu}C_{\mu})CH_{\mu}-$	ن	-0.73457	12457 0-	15721.0-	454474	-(54.51399	12216:0	0.76765	-17.92866	-17.73779	50.04	96'621	22.66	1.94462	0.49298

	Group	O-N C-C	C-O Group	C'H', Group	Group	C-# Group	C - (' (a) Group	C~C (b) Group	ره) کا میس	(p) U-U	(c) (c)	() () () ()
น	2	_	-		2	-	-	-		-		1
7,	0	0	•	2	-	c	-			- ,	-	-
'n.	0	۰	٥	٥	0	0				,	، د	٥
٠,٠	2,0	0.5	0.5	27.0	27.0	0.76		,		3	٥	0
3	 -		-	-			CA	6.3	0.5	50	0.5	0.5
	-	-	- -	- -	- -		-	-	-	-	-	-
	- 000	-	-		-	-	_	-	-	-		-
.,	0.85987	1.06727	0.85395	0.91771	0.91771	0.91771	0.91771	17716.0	17716.0	177160	17716	17710
5	2	٥	٥	o	-	-	0	0	٥	_	-	c
Ş	4	2	2	-		-	2	2	2	2	2	-
	0	0	0	3	2	-	0	0	0	0	0	
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0,5	20
E.	-	-	-		-	-	_	-	_		-	-
r, (aV)	-108,34117	-42,83043	+32.04173	-107.32728	-70.41425	-35.12015	-28.79214	-28,79214	-29.10112	-28.79214	-29 10117	-20 10112
7. (eV)	23.66182	20.48593	9,99436	38.92728	23.78002	12,87680	9,33352	9,33352	9,37273	9.33352	9.37273	9.37773
(65.)	40.95920	12.13739	8.64455	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	005069	6 90400
(46)	-20.47960	-6.06870	4.31232	-16.26957	-10.53337	-5.24291	-5.38732	-3,38732	-3.45250	-3.38732	-3.45250	-3.45250
Aff (m. ch.)	0	-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
יייין ווייין ווייין ווייין ווייין	-0.92918	0	-0.72457	. 0	0	٥	•	0	0	۰	٥	c
(c (c v v) (c V)	0.92918	-15.35946	-13.91032	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15,35946	-15.56407	-15 35946	ANORE 21-
f; (u,sv) (eV)	-63.27057	-31.63327	-31,63537	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	SESES 15-
$F_{T}(atom - atom, msp', AO)$ (eV)	-0.92918	-0.92918	-0.72457	0	0	o	-1.85836	-1.85836	-1.44915	-1 85836	1 44014	1 44016
F. (10) (4V)	-64.19992	-32.56455	-32,35994	-67.69450	-49.66493	-31.63537	-33,49373	-33 49373	-33 08452	-33 40173	23 200 55	Clear.
a (101 rad 1s)	19,2199	23.3578	20.7301	24.9286	24.2751.	24.1759	9.43699	943699	77845	0.62600	-33.00434	7580.00-
Fr (aV)	12.65039	15.37450	13.64490	16.40846	15.97831	15 01700	631169	031169	VP01.01	2,43077	7,33643	9.55643
E, (eV)	-0.22587	0.25261	-0.23648	-0.25352	C105C 0-	D 340KK	0 16616	0.21139	10.19220	6.21159	6.29021	6.29021
F. (aV)	0.20396	0.10725	0.13663	0.35532	0.35522	0.555.0	10113	-0.10515	96807.0-	-0.16515	-0.16416	-0.16416
17.7	[46]	[47]	[21]	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	6) (4)	151	0.12512	0.12312	0.12312
(cr.)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	0 10760
(mag (er)	0.11441	0.13441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
والمراجعة (مراجع)	-64.44771	32,76354	-32.52811	-67.92207	-49,80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33,18712	33.18712
County to an and (cv.)	-14.03489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489
(() () () ()	٥	0	0	-13.59844	-13,59844	-13.59844	0	0	۰	0	0	٥
() (() () () () () () () () (5,67933	76207	2 16017	13 40101								

Exp. 0	٥			110.7	107	(propane) 112 (propane) 113.8 (butane) 10.8	(Putens)	(RODWING)			į	(trobutanc)	11.4	111.4	(addition)
G. B	٤		113.33	11238	101.44	110,49	110,49	109.50	3	1	£.	110.67	111.77	111.27	5
-	Ē							T	T	1				1	1
9	- ©	_													1
9	· ©				_	15.69	1569		20 02		9636				22 50
E,	(§,		-1.44915	-1.44915				0				-1, 43,436	. a	-1 RSR36	
	•		0.86345	0.81549	1.15796			1.13796				Section 5	LOAKR7	1,041687	
ې	•		_	-	0.75			0,75				- 22	67.9	67.0	
Ü			-	-	-			-				- -	-	-	
ű			-	-	-			-					0.75	27.0	
J.	Aim 3		0.91140 (Eq. (15.116))	0.81549	-			-			2.00	17716.0	17716.0	17716.0	
5"	A term I		0,81349	0.81549	0.86359			0.86359			0.000	0,87493	0,87495	0.87493	
Atom 2 Hybridization	Occipation	(Table 15.3.A)	И	**	x			×			×	-	-	-	
Crawterston	Viou 3		-14.53414 N	-16.68411 O,	ī			x			-16,68412	·14.82575	-14,82373	-14.82375	
Atom I Arbridization	Designation	(Tible 15.3.A)	æ	ጃ	,						77	~	*	-	
Frankan	5 KZ	Alon I	71.80(1)	-16,6 x 411	-15,75493			-15.75493			-16.68412	.15.55023	15.53033	.15.55ft73	
2¢'	Alm. (a,)		4.4944	121,4	3,4252			3.4252			4.795x	169.	4.1633	4.7958	
. 5°.	9		2.63661	2.63661	2.11106			117707			7.510.2	211328	2.097(1	2.90327	
Zc,	(%)		2.72270	2.30004	2.11106			2.07711			2,91547	2.91547	291547	2.90327	
Australia Angre			ענס'א	,01,02	H. JHZ	ת'נ"נ"	AC,C,H	ZHC,H	`.'.'.'.'.	H".,".)7	'3''3'.7	H, 7, 72	H, C, 73	سرر"د. مسرر"	15.51.17

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ALKYL NITRITES
$$(C_n H_{2n+2-m} (NO_2)_m, n=1,2,3,4,5...\infty)$$

The alkyl nitrites, $C_n H_{2n+2-m} (NO_2)_m$, comprise a RC-O-NO moiety that comprises C-O, O-N, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise 5 methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is $1s^2 2s^2 2p^4$, and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state 3P_2 . The electron configuration of nitrogen is $1s^2 2s^2 2p^3$, and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state ${}^4S_{3/2}^0$. The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the O-N functional 20 group that is further energy matched to the $C2sp^3$ HO of the C-O functional group. To meet the equipotential condition of the union of the N=O-D functional MO with other orbitals of the molecule, the hybridization factor c_2 of Eq. (15.51) for the N=O-bond MO given by Eq. (15.140) is $c_2(O to N2p to C2sp^3HO) = 0.85987$.

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the N=O bond which requires that two times E_{mag} of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally, $E_T(atom-atom,msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are equal to -0.92918~eV (Eq. (14.513)) which matches the energy of the N=O bond with the contiguous O-N bond and matches the energy contribution of an oxygen atom.

The O-N functional group comprise a single-bond, H_2 -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the $C2sp^3$ HO of the C-O functional group. In alkyl nitrites, the hybridization factor c_2 of Eq. (15.52) for the C-O-bond MO given by Eq. (15.114) is $c_2(C2sp^3HO \ to \ O) = 0.85395$. The hybridization factor c_2 of Eq. (15.52) for a C-N-bond MO given by Eq. (15.116) is $c_2(C2sp^3HO \ to \ N) = 0.91140$. Thus, the hybridization factor c_2 of Eq. (15.52) for O-N that bridges the C-O and N=O bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727$$
 (15.141)

10 $E_T(atom-atom, msp^3.AO) = -0.92918 \ eV$ in order to match the energy of the NO group and $E(AO/HO) = -15.35946 \ eV$ in order to match the C-O functional group.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that $E_T(atom-atom, msp^3.AO)$ and $\Delta E_{H_2MO}(AO/HO)$ are both $-0.72457\,eV$ which matches the energy contribution of an independent $C2sp^3$ HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15,195. The symbols of functional groups of alkyl nitrites.	NO.	N-0	0-0	$C - H \left(C H_{\lambda} \right)$	$C \sim H \left(C \cdot H_3 \right)$	#5	(,~(, (a)	(A)	(3) (, -)	(2)	(a) U)	00.0
Table 15.195. The symbols of	NO group	No	0.0	CH, group	CH, group	₹	CC bond (n-C)	CC bond (Iso-C)	CC bond (tent-C)	CC (iso to iso-C)	(24 812) 23	CC (t to iso C)

Parameter	C/A	N-O	0-0	1.07				1000				
	Group	Group	Group	("") "-"	(cu) /- 1	S S S S S S S S S S S S S S S S S S S	Company of	(a) (a)	(a) (c)	(p) 3-13	(c) (c)	(a)
				Cromo		-		1	4	r r	drain	creap
0 (0")	1.32255	1.76440	1.85327	(.64920	1,67122	1.67465	2.12499	2,12499	2.10725	2.12499	2.10725	2,10725
(, (a,)	1.15002	1,32831	1,36135	1.04856	1.05553	1.05661	1,45744	1.45744	1,45164	1.45744	1.45164	1.45164
Bond Length 3c' (A)	1.21713	1,40582	1,44079	1,10974	£(7)1,1	1.11827	1,54280	1.54280	1.53635	1.54280	1.53635	1.53635
Exp. Bond	1,205 (methyl nitrate)	(methyl nitrate)	1.437	1.107 (C - H propane)		1.12	1.532	1.532	1,532	1.532	1.532	1,532
E	1.2 (HNO ₂)	1.632 (HW2 ₃)	(methyl nitrate)	1.117 (C~H butane)	1.117 (C-H butane)	(isobutane)	1.531 (butane)	(butane)	(putzne)	(Futence)	(buttone)	(propane) 1.531
(a)	0.65314	1,16134	1,25751	1,27295		1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1 57750
5	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	0.68600	0.68600	O. S.R. RRR	OUYBYO	0 60000	000070

and the most of the most of the method generated the parameters of this in this. K.H. If are H or alkyl groups. E., is E. (almir - alone, msp. At)	ממוניםו ממו	וות לשושווירות	danyi lumus.	11 000 11111		1									
Bond	Atom	4	er.	F.	E,	Final Total	[]	Ĩ	Eradon	E(C24)	.0	9	9	ď.	d,
		(eV) Bond 1	(eV) Bond 2	(cV) . Bond 3	(eV) Boud 4	(47.)	(°)	(g)	(S) (E)	(eV) Final	Ξ	· E	Έ	(°)	(0)
RON = 0	9	-0.46459		c	0	(aa)	1 00000	OTTORY	15 2007.4		,	,,,,,			
RON = 0	>	-0,46459	-0.46459	a	0		PEULOU	01910	16 75.03		137.13	37.6	67.90	0.49764	0,63238
RO, -NO,	e [*]	-0,16459	47.36229	ď	0		1,0000	0.86971	15,65263		138,00	16.65	16.48	0.52781	0.62221
RO, - NO.	2	-0,46.159	-0,46459	å	a		0.93014	011910	16.75492		*****		5077	CDGMT 1	0,13925
RH.CO,NO. N = H.alkyl	ť	-0.36229	-0,46459	c	С		1.00000	0.86923	-15.63263		91.43	78.57	47.50	1.19655	0.03173
H,C,, - O,NO,	7.7	-0,36229			۰	151.9779X	0.91771	0,89582	-15,18804	14,99217	93.71	12.98	15.37	67506.1	000
-CH,H,C, - O,NO,	٠٠	-0,36229	1626 D-	c	0	152,907 [6	0,91771	D. Ned X	-16.11723	15.02636	19.16	79.06	42.16	בישנין	567 CH.O.
C-H (CH,)	i.	#16Z6'0"	D	. 0	D	152.54487	17710	0.86339	-15.75493	-13.56407	77.49	16,201	8717	1,23564	O. 1870E
C-H (CH;)	ن	-0.92918	-0 9291K	e .	0	-153,47406	17716.0	0.81549	-16.68412	-16,49325	68.47	111.53	35.84	135486	0.29933
C-H (CH)	ن	-0.0291к	-0.92918	40.9291R	Q	-154,40324	0.91771	0.77247	-17,61330	-17,42244	61,10	118.90	31.37	1.42988	0.37326
H,C,C,L,C,H,- (C,-C, (a))	٠,	-0.9291x			0	-152.54487	0.91771	0.86359	-(5,75493	15.36407	63.82	114.18	30.08	1.85879	0.38106
(C-C (a))	1,5	.0.92918	816200-	e e	o	-153,4740%	17116.0	0.81549	-16.68412	-16,49325	56,41	123.59	26,00	OCKDC.1	0.45117
R-H.C.C.(H.C H')HCH; -	1,0	.0.92918	-0.92918	.0.92918	o	-154.40924	0.91771	0.77247	.17,61330	PAGEN, (1).	48.30	131.70	21.00	91401	100
R-H,C,(R-H,C,)C,(R-H,C,)CH,-	ن	.0.9291R	-0.72457	-0.72457	-0.72457	-154.71860	0.91771	0.75889	22800 71.	1					
(= (((n) n) ncn												67.161	41.14	3,	0.50570
(C-C, (d))	ť	-0.9291¥	\$1626.C-	-0.9291K		-154,40324	17716.0	1+277.0	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	REISO
$(C-C, (R-H_2C_s)C_s(R^*-H_2C_s)CH_1-(C-C, (G))$	۲,	-0.72457	-0.72457 .	-0.72457	-0.72457	-154,51399	17716.0	6.76765	- 17.92xG6	977.77.11	\$0.04	129.96	22.06	1.944/2	0.49258
$lem(L,C,(H,C,-R))HCH_3-(C,-C,(0))$	د.	<i>LSPCL</i> :0-	-0.92918	-0.9291R	۵	-154,19863	17710.0	0.78155	-17,408@	-17.21783	32.78	127.22	24.04	1.92443	0.47279
$BoC_{*}(R-H_{*}C_{*})C_{*}(R-H_{*}C_{*})CH_{*}-$	۲,	-0.72457	-0.72437	40.772457	-0.72457	-154.51399	17716.0	0.76765	.17.92866	-17,73779	50.04	129.96	22.66	1 9463	80,630
77.		_	-					_	-	_	_				

n, n,	3	× - 0	o-0	ίχ.)	÷.	<i>H</i> − 0	(g)	(a)	(S) (-) (-) (-)	(G)	(e) ∪-∪	(E))-'
n _c n _c ,	dneo	cont	Cronb	Group	Group	Group	Group	Group	Group	Group	Group	Group
n,	2	1	_	m	2	1	-	_	-	_	-	_
	0	0	0	7	_	0	0	0	٥	0	°	o
n,	o	0	0	0	0	0	0	0	0	0	٥	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	29
ر.:	-	_	-	-	_	1	-	-	_	_	1	-
c,	-	-	-	-	-	-	_	-	-	1	-	-
ŝ	0.85987	1.06727	0.85395	0.91771	17416.0	17710.0	0.91771	17716.0	0,91771	0,91771	17716.0	17716.0
.,	2	0	0	0	1	1	0	۰	٥	-	1	
د.	4	2	3		-	-	2	2	2	2	2	2
ŗ.	٥	0	0	3	2	1	0	0	0	٥	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	_	-	1	1	1	1	-	-	_	-	1	-
V, (cV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29,10112
V, (eV)	23.66182	20.48593	9,99436	38.92728	23.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9,37273	9,37273
' (eV)	40.95920	12.13739	8.64465	32,53914	21.06675	10.48582	6,77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-20.47960	-6.06870	-4.32232	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(** m) (*V)	0	-15.35946	-14,63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
DE nime (in no) (oV)	-0.92918	0	-0.72457	. 0	0	0	0	0	0	0	0	0
Er(40 10) (eV)	0.92918	-15.35946	-13,91032	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
F. (u,in) (eV)	-63.27057	-31,63527	-31,63537	-67.69451	-49,66493	-31.63533	-31,63537	-31.63537	-31.63535	-31,63537	-31,63535	-31,63535
$E_{\tau}(\alpha tam - \alpha tom, nesp', AO)$ (eV)	-0.92918	-0.92918	-0.72457	. 0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
F. (10) (CV)	-64.10992	-32.36455	-32.35004	-67.69450	-49,66493	-31.63537	-33,49373	-33.49373	-33.08452	-33,49373	-53.08452	-33.08452
a (1012 rad 1 x)	19,2199	23,3578	20.7301	24,9286	24.2751	24.1759	9.43699	9,43699	15.4846	9,43699	9.55643	9.55643
F. (eV)	12.65089	15.37450	13.64490	16.40846	15.97831	15,91299	621159	6.21159	10.19220	6.21159	6.29021	6.29021
E, (uV)	-0.22587	0.25261	-0.23648	-0.25552	-0.25017	-0.24966	-0,16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
(h)	0.203%	0.10725	0.13663 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.12312	0.1797 8 [4]	0.09944	0,12512	0,12312	0.12312
E., (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
F. (aV)	0.11441	0.11441	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803
E_ (name) (cV)	-64.44771	32,76354	-32.52811	-67.92207	-49,80996	-31.70737	-33.59732	-33.49373	-33.24376	-33,59732	-33.18712	-33,18712
French (. es 173) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Frank, in my (dV)	0	0	0	-13,59844	-13.59844	-13.59844	0	0	0	0	0	•
Enfrant (cV)	5.67933	3.49376	3,25833	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

(;-C (e)

Table 15.199. The total band energies of alkyl nitries calculated using the functional group composition and the gnergies of Table 15.198 compared to the experimental values [3].

Formula Name Name Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group Group

			-							_				
	Exp. θ		110.7 (FNO,)	107 (propane)	112 (propane) 113.8 (bulone) 110.8 (replutace)	[butma] 111.4 Genhudane]	7			1 IQ.R (Ssobutane)		(fsobutare)	III.4 (Isobutane)	
	Cal. θ	113,33	112.38	101.44	110.49	110.49	109.50	109.44	100.44	110,67	110.76	17111	111.27	93.60
	6,0													T
	ø. O													T
	o, ©				15.09	1569		70.56	70.56					5
	E _T (e.V.)	-1.44915	-1.44915	0			c			-1,85836	0	0	-1.8383%	
om, msp' AO).	~	0.86345	0.81549	1.15796			1.15796			6P\$18'0	(,048R)	1,04837	1.04887	
$E_r(atom - ot$	3	-	-	0.75			0.75			-	6.75	0.75	67.0	
scd. E, is 1	Ç	-	-	-			-			_	-	-	-	
ngle were ur	υ	-	-	-			_			-	0.75	6.75	0.75	
ie preceding ar	C ₂	0,91340 (Eq. (15.116))	0.81549	-		l	-			0.81549	17710.0	17716.0	1/1/16,0	
meters from th	C ₃ Alson I	0.81549	0.81549	0.86359			0.86359			0.81549	0.17495	0.87495	0,87405	
tion of 0, the pare	Atom 2 Hytridization Designation (Table 15.3.A)	l i	77	π			#			ุล	-		_	
in the calcula	Erusham Ann 2	-14.53414	-16.6K411	Ξ			н			-16,6K412 C.	-14,82575	-14,82575	-14,82575 C,	
nental values [1].	Atom 1 Hybridization Designation (Table 15.3.A)	ľ I	22	,			^			я	*I	\$	\$	
and experin	Erahanta or E	-16,68413	0	-15.75493			-15,75495			-16.6KH12	ر" -۱۶.53033	7.)	-15.55053	
ikyl nimites	2c' Tomètel Abere (G _b)	4,4944	4.1331	3,4252			3,432			4.795#	4,1633	¢ 1633	4,795R	
ameters of a	2c° Bond 2 (0 ₀)	1.65661	2.65661	7.11106			2,09711			2.91547	2.11323	2.09711	2,90327	
nd angle par	2c' Bmd I (a _b)	2.722.70	2.30004	2.41106			2,09711			2.91547	291547	2.91547	2.90327	
ablo 13.400. The bond angle parameters of alky a intries and experimental values [1]. In the calculation of 0, the parameters from the preceding angle were used. E, is E, (atom - atom, myp' AO)	· Awer of Atglo	דנמ'א	ZO,NO,	H JH7	מניני.	H,","	H_JH7	קניני: קניני:	H' ', ',	7, 7, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	4C,C,H ™ C,	, m C, H	אמע ני" קניני, ני"	15.5.7

ALKYL NITRATES $(C_n H_{2n+2-n} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$

The alkyl nitrates, $C_n H_{2n+2-m}(NO_3)_m$, comprise a $RC-O-NO_2$ moiety that comprises C-O, O-N, and NO_2 functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups (CH_3) at each end of the chain, and may comprise methylene (CH_2) , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl $((CH_3)_2 CH)$ and t-butyl $((CH_3)_3 C)$ groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The NO_2 functional group is equivalent to that of nitro alkanes with the exception that $\Delta E_{H_2MO}(AO/HO)$ as well as $E_T(atom-atom,msp^3.AO)$ is equal to -3.71673 eV in order to 15 match the group energy to that of the contiguous O-N bond. Furthermore, the O-N group with $E_T(atom-atom,msp^3.AO) = -0.92918 \, eV$ is equivalent to that of nitrites as given in the corresponding section.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that $E_T(atom-atom, msp^3.AO)$ and $\Delta E_{H_1MO}(AO/HO)$ are both 20 -0.92918 eV which matches the energy contribution of an independent $C2sp^3$ HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 25 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

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115 SYMOOIS O	and the symbols of fundional groups of alkyl nitrates.
Functional Group	Group Symbol
NO, group	NO.
2.0	, × - C
S	;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;
CH, group	$C-H$ (CH_3)
CH, group	C-H (CH.)
픙	
CC bond (n-C)	(8) (7-1)
CC bond (iso-C)	(a) ()
CC bond (tert-C)	(3)
CC (iso to iso-C)	(2) :
CC (1 to 1-C)	(a) (a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c
CC (t to iso-C)	(S) .: -: :

Table 15.202	Table 15.202. The geometrical bond parameters of alkyl nitrates and	ond parameters of al	lkyl nitrates and exp	experimental values [1].								
	AO2, Group	Group	O LO	Groun	$C-H(CH_1)$	Group	C-C (a) Group	C-C (b)	(c-C (c)	(p) 2~2	(a) 2-2	(J-)
$\sigma\left(a_{0}\right)$	1.29538	1.76440	1.83991	1 64970	CE179.	25.65			dnoin	Ciroup	Group	Group
c. (o')	1.13815	113611	13663		77110	1.0/403	2.12499	2.12499	2,10725	2.12499	2.10725	2 10725
Bond		10070	1,33043.	1.04856	1.05553	1.05661	1.45744	1.45744	1 45164	1,4574,4		
1									10101	1.43/44	1.45164	1.45164
2c' (A)	1.20456	1.40582	1.43559	1.10974	1,11713	1,11827	1.54280	1.54280	1.53635	1,54280	1.53635	31,313
Exp. Bond	1.205	1.402		101								Corre
Length	(methyl nitrate)	(methyl nitrate)		(C-H propane) (C-	(C - H propane)	1.122	1.532 (oropane)	1.532	1.532	1.532	1.532	1.532
9	(HNO ₂)	(<i>HNO</i> ₁)	(meinyi nitrate)	1.117 (C-H butane)	1.117 (G = A butane)	(isobutane)	1.531	1.531	(proparte) 1.531	(propane) 1.531	(propane)	(propane)
h,c (a,)	0.61857	1.16134	1.24312	1 27305	(2000)		(Dutane)	(butane)	(butane)	(butane)	(butane)	(butane)
v	0.87862	0 75284	27777	65757	69067.1	1.29924	1.54616	1.54616	1.52750	1.54616	1 57750	
			0,13123	0.60.580	0.63150	200530	00,000				20170	1.74/30

	İ							•							
Bond	Атош	E_T	£,	E,	If.	Final Total		<u>[</u> 3	Eraubas	$E(C2sp^3)$.0	6	9,	ď,	9
		(eV) Bond 1	(eV) Bond 2	(cV) Bond 3	(eV) Bond 4	Czyp ²	ં.	(%)	(eV) Final	(cV) Final	ေ	©	· ©	(°)	(a)
RV(O) = O	9	.0.7291X	0		ė		00000 1	0.86359	.15.75493		13x 49	15 17	02.69	277100	0 6467
RN(O) = O	2	81626.0-	\$1676'U-	41,464.59	6.		0,93024	0.79340	.17.14K70		135,60	6.12	63.83	E1/20	0.56682
RO, - N(O,),	70	-0.46459	6SPYPIT-	c	-		1.00000	0,16359	-15.75493		94.78	27.13	47.30	1.19635	0.13175
RO N(O.);	N	-0.46459	\$1676'th	-0.9291K.	c		0,93014	0.79340	-17,14870		92.78	17.73	43.03	1,28978	0,03852
$RH_2C_s - O_sN(O_s)_s$ $N = H_salk_3^s$	**	-0.46459 -	46459		c		1,0000	0.46359	-15.75493		51.59	\$7.87	43.9%	132431	0,03212
H,C, -O,N(O,),	C.	-0.46459	0	e	0	-152.0R028	17719,0	CKURA.0	- 15.20034	115.00948	9576	15.64	\$.55	(,28872	17790,0
-CH, H, C, -O, N (O,),	ن	-0.414.59	-0.0291K	0	0	-153,00946	0,91771	0.83#85	-16.21952	-16,02866	19.90	90.10	44	1.3578.7	0.00143
< H (CH,)	Ü	-0 929 LK	0	C	0	.152.StuR7	17116.0	0.86359	-15.75493	-15.56407	77,459	15.201	41,48	1,23564	Q. IKTOR
C-H (CH;)	Ü	-0.92918	41,92918	. 0	0	-153,47406	0.91771	0.81549	-16.68412	-16,49323	68.47	111.53	33.84	1,35486	0.29933
C - H (CH)	ij	-0,9291k	-11.9291X	.0.92918	0	-154.40324	0,91771	T1277.0	.17.41330	-17,42244	61,10	118.90	11.37	1.42988	0.37326
H(',',',',',',',',',',',',',',',',',',',	C,	N1020,0-	0	o .	O	. 132 Statk7	17719.0	0.86359	-15.75403	13,56,407	63.82	116.18	30,00	1.83879	0.38106
H.C.C.H.CH.; (CC (a))	5)	-0.929 IR	#16764r	0	0	-153,47406	1771g.d	0.81549	-(6 68412	-16,40325	36.41	92.63)	26.06	058061	0,45117
$R = H_3C_3C_4(H_3C_4 - R^2)HCH_3 - (C' - C'(b))$	٠٠٠	-0.9291K	*16291J-	ж1626.0-	۰	134,4024	17710.0	0.77247	-17,61330	-17.42244	44.30	131.70	21.90	1,97162	0.51318
$R = H_2C_a(R^2 - H_2C_a)C_a(R^2 - H_2C_a)CH_2 - (C - C_1C_0)$	ú	.0.9291x	-0.72457	-0.72457	-0.72457	-154.71860	0,91771	0.75889	-17.92866	04767,71-	4121	131.79	21.74	HE780.1	0.50570
μος,ς,(Ή ₂ ς, - R') ΗCH ₂ - (CC' (d))	ر.	x10560.	x 1676 U-	ж (седе-	9	-154,41324	17719.0	0,77247	.17.61330	b450.71.	48.30	131.70	21.90	1,97162	0.51388
$\operatorname{unK}_{\sigma}(R-H_{\delta}C_{\sigma})C_{\sigma}(R^{n}-H_{\delta}C_{\sigma})CH_{\sigma}-(C-C^{-}(\mathbf{e}))$	ن	-0.72437	-0.72457 .	. 0.724S7	-0.72457	C(E(\$)\$1-	0,91771	0.76763	-17.92866	errer.11-	\$0.04	120.96	22.66	1,54462	0.49298
$min'.C_*(H_2C_* - R')RCH_2 - (C-C, \{0\})$	٠,	-0,72457	к 1626 О-	81626.0-	4	.154,19863	0,91771	0.78155	-17.40869	-17,21783	82.78	17771	24.94	1,92445	0.47279
$kwC_{*}(R^{*}-H_{3}C_{*})C_{*}(R^{*}-H_{3}C_{*})CM_{3} (C-C_{*}(0))$	ť	-0.72457	15921.0-	-0.72457	-0.72457	.154.51399	0.91771	0.76763	.17.92866	-17,75779	50.04	129.86	22.66	1.9462	0.49298

Table 15.203. The MO to HO intercept geometrical board parameters of alkyl airmites. R.R.R. R" are H or alkyl groups. F, is E, [anun-ation, mgr. Att).

[Bond

	Seg.	Organ	O-0	GH,	ξ,	Group	CC. (a) Group	C C (b) Greup	(c) (c)	C-C (d)	(e) C-C (e)	(F) O-C
,	2	-	-	1	2	-			-	-	dans	de)
12,	0		o	2	-				- -	- -		-
п,	0	0	0	0	6		6	,	,			}
	0.5	ř	•	2,0	35.0	35.0	, ,	, :	,	2		3
÷		3	3		67:0		Ca	6.3	6.5	0.5	0.5	0.5
*		-	-	-	-	-	-	-	-	1	- 1	-
	-	-	-	-		1	-	_	_	-	1	-
	0.85987	1.06727	0.85395	0,91771	17710.0	17716.0	17716.0	0.91771	17710	17716.0	17710	122160
i	٥	0	0	0	1	-	0	0	0	-	-	0
	4	2	2	•	1	-	2	7	2	2	2	-
	0	0	0	3	2	_	٥	o	0	0	0	
4	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.3	0.5	0.5	0.5
	-	-	-	-	-		1	-	-	-	-	-
V_ (eV)	-112,63415	-42.83043	-32,35681	-107,32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V (cV)	23.90868	20.48593	10.03058	38.92728	25.78002	12.87680	9.33352	9,33382	9.37273	9.33552	9.37273	9.37273
(aV)	43,47534	12.13739	8.79304	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6 90 500
V_ (eP)	-11.73767	-6.06870	-4.39652	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	3.45250
El. a 10) (cV)	ò	-15,35946	-14.63489	-15.56407	-15.56407	-14.63489	.15,36407	-15.56407	-15.35946	-15,56407	-15.35946	-15,35946
D'uzar (et m) (cV)	-3.71673	0	-0.92918	0	0		0	0	0	o	0	0
E, (r. m) (eV)	3.71673	-15,35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
F. (u, w) (aV)	-63.27107	-31,63527	-31.63542	-67.69451	-49,66493	-31.63533	-31,63537	-31,65537	-31,63535	-31,63537	-31.63535	-31,63535
$E_T(atom - atom, msp', AO)$ (cV)	-3.71673	-0.92918	81626'0-	0	0	0	-1.85836	-1,85836	-1.44915	-1,85836	-1,44915	-1.44915
E, (un) (cV)	-66.98746	-32,56455	-32.56455	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
a) (10" rad/s)	19.8278	25.3578	21.0910	24,9286	24,2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
£, (aV)	13.05099	15.37450	13.88249	16.40846	15.97831	15.91299	6.21159	621159	10.19220	6.21159	6.29021	6.29021
K, (eV)	-0.23938	0.25261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16513	-0.20896	-0.16515	-0.16416	-0.16416
f. tra (eV)	0.19342	0.10725	0.15663 [21]	(Eq. (13.458))	0.35532 (Eq. (13.458))	0.55532 (Eq. (13.458))	21521.0	0.17978	0.09944	0.12312	0.12312	0.12312
E (eV)	-0.14267	0.19899	-0.17172	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	0.10260
E (cV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
F. b (OV)	-67.27281	32.76354	-52.73627	-67,92207	96608'65-	-31,70737	-33.59732	-33,49573	-33.24376	-33.59732	-33.18712	-33.18712
12 man (s. 40 177) (UV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
E (1, 10 110) (cV)	0	0	0	-13,59844	-13.59844	-13.59844	0	o	e	0	0	0
(25) (at)	8.73325	3.49376	3.46649	12 49186	71016	103654	1,000	1				

(i) 2-2

	Exp. 9	E		(methyl nitrae)	103 (mathyl nitrate)		(18.1 (methyl mirate)	(methyl nitrate)	(methyt nitrate)	107 (prepane)	112 (propanc) 113.8 (butanc) 110.8 (secoutanc)	(butant)				110.R (trobutane)		(tsobutane)	111.4 (cschalane)	
	Cal. 0	E	109.50	100.44	100.68	129.83	115.09	(Eq. (15.99))	112.79	108.44	110.49	110,49	109.50	109.44	100.44	110.67	110.76	111.27	111.27	107.50
	6	©.																		
	6	©					129,83	129,83												
	0,	• •		70.56							1569	1509		70.56	70.56					2.50
<i>10</i>).	E,	<u> </u>				-1,44915			-1,44915	0			•			-1.85836		٥	-1.85836	
– atom, msp².,	٧.		1.15796		0.93052	0,81549			0,16345	1.15796			1.15796			0.81549	1,04117	1,04177	1.04887	
is E _r (afom	ن		87.0		873	-				67.0			0.75				0.75	475	0,75	
used. E.	5		-	L	_	_			-	_			_			-				
angle were	<u>5</u>	. —.	_		27.0	-			-	-			-			-	27.0	0.75	57.0	
an the preceding	5	7 mayor	-		0,15395 (Eq. (15.114))	0,81549			0.91140 (Eq. (15.116))	-			,			0.11549	0.91771	1,771,00,0	Q91771	
he parameters fro	5		0.86359		17716.0	0.81549			0,81549	0.86359			0.K6359			0,81540	0,17495	0,N7405	0,87495	
alculation of θ_{\star} , t	Aton 2 Hybridization	Designation (Table 15.3.A)	Ι		0	7.			z	×			Ξ.			. 22	-	-		
[1]. In the c	E. come	į	. =		-13.618706	-16,68411°		i	-14.53414 N	π			н			-16,68412 (°,	-14.K2575	-14.R2575 C,	-14.K2575	
enmental values	Atom 1 Hybridization		1	*	-	*			ุ่ม	,	•		4			ñ	•	•	8	
ates and exp	E.	ا ا د د	-15.73493		-14.82575	-16.68411 O			1.) 21 31 91-	-15.75403			-15.75493			1.3 2122993	.15 55033 (°,	-15.55033	-15.35033 C.	
of alkyl nitr	2¢'	j &	34252		1.72.F	4.1231			4,4721	3.4252			tstrv			#\$'64' ₱	4.1633	4.1633	4 7958	
arameters (77.	<u>કે</u>	2.09711		2,71287	2,27630			2.65661	2.11106			2.09711			27516.2	πειιτ	112607	2.90327	
ond angle i	.2.]	(°	11790.5		1,09711	2,27630			2.71287	2.11106			2.09711			1.91547	1.91547	191547	1.90327	
Table 15.206. The bond single parameters of alkyl nitrates and experimental values [1]. In the calculation of $ heta_c$, the parameters from the preceding angle were used. E, is E, (atom - atom, msp*AO)	Alvena of Anglo		ZHC.H	0.7.HZ	'0",5"H7	, אייטי <i>ב</i>	CO NO	CO,NO,	<i>ห</i> ืบ <i>ว</i> 7	H".)H7	75.55	H'.5".17	H".JH7	75.5.57	H'. 5. 17	بيدر." حرياريور	H'.J'.H H'.J'.E	ZC., C.H.	ZC,C,C,	, J', J', J'

CYCLIC AND CONJUGATED ALKENES

$$(C_n H_{2n+2-2m-2c}, n=3,4,5...\infty, m=1,2,3..., c=0 \text{ or } 1)$$

The cyclic and conjugated alkenes are represented by the general formula $C_nH_{2n+2-2m-2e}$, $n=3,4,5...\infty$, m=1,2,3..., c=0 or 1 where m is the number of double bonds 5 and c=0 for a straight-chain alkene and c=1 for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent 10 fragments, and differences in oscillation in the transition state, five distinct C-C functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition, CH_2 of any $-C=CH_2$ moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group (CH_3) , and may comprise methylene (CH_2) , and methylyne 15 (CH) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The C-C groups are solved in the same manner as those of the 20 branched-chain alkanes given in the corresponding section. For example, the cyclopentene $C_a - C_b$ group is equivalent to the n-C-C alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of H from the terminal methyl and methylene groups. Thus, the energy of each of 25 the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene $C_c - C_d$ and the cyclopentadiene $C_a - C_b$ groups is the magnetic energy (Eq. (15.58)) which is subtracted from the $C_a - C_b$ total bond energy according to Eqs. (13.524-13.527) due to the formation of a CH group from the methylene group.

 $E_T(atom-atom, msp^3.AO)$ of the C=C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, $-2.26759 \, eV$, given by

Eq. (14.247). $E_T(atom-atom, msp^3.AO)$ of each C-C-bond MO in Eq. (15.52) is $-2.26759 \, eV$ or $-1.85836 \, eV$ based on the energy match between the $C2sp^3$ HOs corresponding to the energy contributions equivalent to those of alkene, $-1.13379 \, eV$ (Eq. (14.247)), or methylene, $-0.92918 \, eV$ (Eq. (14.513)), groups, respectively, that are contiguous 5 with the C-C-bond carbons. In the former case, the total energy of the C-C bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of 0.5e must be donated to the C-C bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the C-C-bond MO and increases the C-C bond energy. This additional lowering of the C-C-bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) 15 parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum 20 of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.

Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.	oups of cyclic and conjugated alkenes.
Functional Group	Group Symbol
CC double bond	ر=ر
1,3-butodiene, 1,3-pentadiene (", - (',	
1,3-cyclopentadiene ('(',	(B)
La-pentadiene (; -(',	6 0 0
cyclopentene (',(',	(0)
1,4-pentadiene (', -(',	(,-(,(c)
1,3-cyclopentadiene (', - (',	(p)
cyclopentons (((e) (c)
CH, alkenyl group	$C = H\left(CH_2\right)$ (i)
CH, group	C - H (CH ₃)
CH; alkyl group	$C - H\left(CH_{2}\right)$ (ii)
CH	H)

360590	63189	0.63580	0.63756	0.68600	0.69887	0.69887	0,69887	0.72309	0.86030	10
1.29924	1.29569	1,27295	1.26354	1.54615	1.46439	1,46439	1.46439	1.32110	0,75035	h,c (a,)
1.122 (isobutane)	(C - H propane) 1.117 (C - H butane)	(C - H properte) 1.117 (C - H butane)	(2-methy propenc) 1, 108 (avg.) (1,3-buadenc)	(cyclopentens)	(1,3-cyclopentadiene)		(cyclopentene)	1.469 (1.3-cyclopentadiene)	(1,3-cyclopentadiene)	(x)
l	1.107 (C - H propane)		1.10 (2-restavleronene)	1.546	1.509		915.1	1.467 (1,3-butadiene)	1.349 (1,3-butadiene) 1.342	Exp. Bond Length
1.11827	1.11713	1.10974	1.10668	1.54280	1.51437	1.51437	1,51437	1,46365	1.34052	Bond Length $2c'(A)$
1,05661	1.05553	1.04856	1.04566	1,45773	1,43087	1,43087	1,43087	1.38295	1.26661	c. (a,)
1.67465	1.67122	1.64920	1.64010	2,12499	2.04740	2.04740	2.04740	1.91256	1.47228	a (a _o)
Group	Group	Group	(i) Group	Group	Group	dago	dingo	dioin	diago	
11-0	C-H (CH,)	L	C-H (CH2)	(a) U-U	(p) .) - U	(a)	(a)	(*)) e ()	Parameter

Bond	Atom	الج (aV) Bond ا	lí _r (eV) Bond 2	β,τ (aV) Bond 3	E _T (eV) Bond 4	Final Total Energy (.2sp² (eV)	(%)	('p)	Enal(C14) (eV) Final	E(C2sp³) (eV) Final	(•) .0	, (°)	(•)	(°a)	(a, c,
$H_1C_1 = C_1(H)(H)C_1 = CR$ $(1.3-but odium_4, 1.3-pantadium_5)$ $H_1C_2 = C_1(H)C_1H_1C_1(H) = C_2H_1$ $(1.4-pantadium_5)$	ن	-1.133KD	c	•	B	GrGr£251-	122160	0.85252	-13.93953	-13,75868	122,84	30.16	60.70	0.77200	0.54620
$H_2C_a = C_a(H)(H)C = CR$ (1.3-butadiena, 1.3-pantadiena) $-HC_a = C_c(H)(H)C_c = C_aH =$ (1.3-exylopentadiene)	3 0	-1.13380	-1,170%	8	3	#ZD&(151-	17716.0	70267.0	-17,00334	81700391-	127.13	TA CA	t.R	o.78613	0.48047
$H_{\mathcal{L}'_{+}} = C_{+}(H)(H)C_{+} = C_{-}(H)C_{+}H,$ $(1.3-pantadiene)$ $H_{\mathcal{L}'_{+}} = C_{+}(H)C_{+}H,C_{+}(H) = C_{+}H,$ $(1.4-pantadiene)$ $-HC_{+} = C_{+}(H)(H)C_{+} = C_{+}H -$ $(1.3-cyclopantadiene)$ $-H_{\mathcal{L}'_{+}}C_{+}(H)(H)C_{+} = C_{+}H -$ $-H_{\mathcal{L}'_{+}}C_{+}(H)(H)C_{+} = C_{+}H -$ $-H_{\mathcal{L}'_{+}}C_{+}(H)(H)C_{+}(H) = C_{+}H -$ $-H_{\mathcal{L}'_{+}}C_{+}(H) = (H)C_{+}C_{+}H -$	ಆಆಆಆ	-1,13340	*1.0\$6'(r	e	=	-131,67867	0 21771	0.30361	-16,83873	òκΓ¢),∂!-	127.61	52.39	5K.24	0.77472	891Gr'0
$RC = C_{\infty}(H) - (H)C_{\infty} = CR$ $(C - C_{\infty}(B))$, r,	-1.1380	-1.1338u	=	a	-453,M32X	17710.0	0.77597	4000,TI-	NFZ0G:91-	16.87	(9'10)	36.16	81#151	0.16123
$H_{f,c} = C_{s,f}HC_{s} = C_{s}(H) - C_{s}H_{s}$ $(1,2-pensatione)$ $-H_{f,c} = C_{s}(H) = (H)C_{s} - C_{s}H_{s} - (psyloppatione)$ $(C-f, 0)$	ਹ ਦ	-1.13340	и (СТО) Э	e	0	-183,67467	17.14.0	19K1340	- 16.808.73	-16.037WG	64.37	£4.211	W.01	L.7KSH	965-€0
$H_2C_p = C_k(H)(H)C_k = C_k(H) - C_pH_2$ (1,3-pertudiene) (C - C (b))	Ů	81226'B-	c	С	c	-152 54.187	17710.0	0.KG599	-13.75400	-15,56407	ינגה	197,73	34.17	.@JKK	10032.0
$-H_*C_* - C_*(H) = (H)C_* - C_*H_* - (Cyclopentne)$ (Cyclopentne) (C - C_*(b))	ڻ	-0,9291X	40,92918	e	G	-(53,47405	177.16.0	0,81549	-16.68413	-16,40325	65.99	114.01	30,5%	0,76270	DIE O
$H_{s,s}^{c} = C_{s,s}^{c}(H) - C_{s,s}^{c}(L) = C_{s,H}^{c}$ (1, 4-peniadiene) (1, 2-c, 6) $-H_{s,c}^{c} - HC_{s,s}^{c} = C_{s,H}^{c} - C_{s,H}^{c}$ (1, 2-expensadiene) (1, 2-c, 6)	υ υ	-1,13340	K 62673-	÷	•	-153.67kG6	17716.0	0,47561	CZ88791-	-16.60786	G4.57	115,43	£.62	1.77684	0,34396
$H_i C_s = C_s(H) - C_s H_i C_s(H) = C_s H_i$ (1.4-pounations) $(1.6 - C_i C_i)$ $- H_i C_s - H C_i = C_i (H) (H) C_s = C_i H - H_i C_s - C_i H$ $(C_i C_i (d))$	Ú 6	×1626.0-	-4,9291X	=	٥	50:71-551-	17716,0	CASIK.0	. 1146,6411	-16.43323	8 .39	16,01	30.58	1.7%270	033183
$-H_1G_+ - H_2G_*G_*(H) = (H)G_*G_*H_1 - G_*G_*G_*H_2$ (eyelopentene) $(G = G_*(e))$	575	41.0 <u>27</u> 3.11K	M162617	s		-153,47403	17710.0	0.81549	-16,68411	-16 49325	\$6.41	811	26.06	1.50890	0,45116
C - H (CH;) (i)	ij	-1.133HQ	0	a	0	-152,71949	17716.0	0,85252	-13.93955	-15.7686Я	77.15	10285	41.13	12331	0.18765
с-н (сн.)	υ	KI GZU-II-	0	c	0	-152.54487	17716.0	0.80350	-13.75473	-15.56407	77.49	102.51	41,48	1,23564	0.18709
C - H (CH ₁) (ii)		X1626'0-	# 676't)-	0	0	-153,47406	17716.0	0.8154.0	-16.68412	-16.49325	GK.47	111.53	35.84	1.35486	0.29333
C-H (CH)	·	*ICCC+	-0.9291R	H167.00-	•	14131	100		2000	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,					

Parameters	C=C Group	('-(' (a) Group	('-(' (b) Group	(: - (' (c) Group	C:-(' (d) Group	C~C (e) Group	CH, (I) Group	CH, Group	CH, (ii) Group	C-H Group
u u	2	_		-	-	-	2	3	2	1
<i>n</i> ;	0	0	0	0	0	0	1	2	1	o
n,	0	0	0	0 .	0	0	0	0	0	0
5	0.5	0.5	0.5	6.5	0.5	5.0	0.75	0.75	0.75	0.75
6,	0.91771	-	-	-	-	-	ı	-		-
5	-	_	-	-	_	_	_	_	ı	-
່ນ	0.91771	0.91771	17716.0	0.91771	17716.0	0.91771	0.91771	0.91771	17716.0	0.91771
-5-	0	0	0	0	-	0	-	0	-	1
5	4	2	2	2	2	2	_	-	-	_
ű	0	0	0	0	0	0	2	3	2	1
(;	0.5	0.5	0.5	0.5	0.5	6.5	0.75	0.75	0.75	0.75
	0,91771	-	-	-	-	-	-		_	1
V, (eV)	-102.08992	-33,01226	-30,19634	-30,19634	-30.19634	-28.79214	.72.03287	-107.32728	-70.41425	-35.12015
V, (aV)	21.48386	9.83824	9.50874	9.50874	9.50874	9.33352	26.02344	38.92728	25.78002	12.87680
T (eV)	34.67062	8.63041	7.37432	7.37432	7.37432	6.77464	21.95990	32,53914	21.06675	10.48582
V_ (uV)	-17,33531	-4.31520	-3.68716	-3.68716	-3.68716	-3.38732	-10.97995	-16.26957	-10.53337	-5.24291
E(40 to) (aV)	0.	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$\Delta E_{n_p,top}(.o.in)$ (cV)	0	-1.85836	0	0	o	0	0	٥	0	0
Er (101 10) (CV)	0	-12.77653	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
$\mathcal{E}_{r}[u_{i}\omega](aV)$	-63.27075	-31,63535	-31.63534	-31.63534	-31.63534	-31.63537	-49.66437	-67.69451	-49.66493	-31.63533
$\mathcal{E}_{r}\left(a_{10}m-a_{10}m,msp^{3},AO\right)\left(eV\right)$	-2.26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0	0
E, [sn] (eV)	-65,53833	-33.90295	-33.49373	-33.49373	-33,49373	-33.49373	-49.66493	-67.69450	-49.66493	-31.63537
ω (10°° rud / s)	43,0680	11.0522	15826.6	1625.52	15826'6	9.43699	25.2077	24.9286	24.2751	24.1759
E_{κ} (σV)	28,34813	7.27475	6,56803	15,35563	6.56803	621159	16.59214	16.40846	15.97831	15.91299
Γ, (eV)	-0.34517	-0.18090	-0.16982	-0.25966	-0.16982	-0.16515	-0.25493	-0.25352	-0.25017	-0.24966
Ex., (eV)	0.17897 [6]	0.14829	0.11159	0.11159	0,11159 F121	0.12312	0,35532 Eq. (13,458)	0.35532 Eq. (13.458)	0.35532 Eq. (13,458)	0.35532 Eq. (13.458)
E_ (aV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.11402	-0,10359	-0.07727	-0.22757	-0.14502	-0.07200
E (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (kimus) (cV)	-66.04969	-34.00972	-33.60776	-33,69760	-33.60776	-33.59732	-49.81948	-67.92207	-49.80996	-31.70737
E, was (4, 4) 10) (cV)	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
Eimalle, to 10) (cV)	0	0	0	0	0	0	-13,59844	-13.59844	-13,59844	-13.59844
Eplimal (eV)	7.51014	4.73994	4.33798	4.42782	4.18995	4.32754	7.83968	12.49186	7.83016	3,32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy E___ that is subtracted from the

eighted sun	veighted sum of the $E_{\mu}(\omega_{\mu\nu})$ (4 V) values base	values base	sadiuoo no ba	ition is given	by (15.58).									•	
ormula	Мате	ر=ر د=ر	(, – (, (a)	(, -(. (p)	()-(; (e)	(, - (, (q)	(a) (b)	(H, (i)	, 55	CH, (ii)	£	in the	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative
	1 Butadiene	2	_	•	0	0	0	7		0	2		42.09159	42.12705	0,00084
C. H.O	1,3 Pentadieno	7	-	_	٥	0	0	_	-	٥	0	,	54,40776	54,42484	0.00031
	Pentadiene	~ 1	0	•	2	0	0	۲)	٥	_	7	٥	54.03745	54,11806	0.00149
	Cyclopentadiene	r)	-	•	0	~	0	•	۰		₹	۰	49.27432	49,30294	0.00051
	donentana	_	_	•	•	c	•	•	-	~	•	-	59514 75	\$4 B6117	7,000,0

	, ,					41				
Exp. θ (•)		120.9 (1,3-butadiene)	(anaibalud-E,1)	(1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-burations CCC) (1.3-b	109.4 (1,3-cyclopentadiene)	1,3-cyclopentadiene)	102.8 (1,3-cyclopentadiene)	110.0 (cyclopentene)	103.0 (cyclopentene)	104 0 (cyclopentene)
Cal. 9	113.25	123,38	119.45	126.48	108.44	108.47	1077.01	110.14	102.85	103.61
ø,©										
e. C		113.25				-				
θ, (C)										
E_T	0		0	.1.85836	-1.85836	-1,85836	-1,85836	-1.85836	-1.83836	-1.85836
ን'	1,17300	·	00000'1		0.76360	-74477-0	0,78155	10.777.0	0.78620	0.79085
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ປົ	-		0.75	-	-	-	-	-	-	_
C; Arem ?	1		0.85252	0.79597	0.76360	0.77247	0.78155	0.77247	0,78155	0.79085
C ₂	0.85252		0.85252	0.80561	0.76360	0.77347	0.78155	0.78155	0,79085	0.79013
Atom 2 Hybridization Designation (Table 15.3.A)	н		6	. 30	25	4	38	\$	38	×
Eradonder Alem 3	ж		-(5,9595d	1,709334	-17.81791 C.	-17.61330 C.	-17,40869	-17,61330	-17,40869	-17,20408
Atom Hybridization Designation (Table 15,3.A)	6		6	. 11	94	4	38	80	3,5	35
Erande Amel	-15.05955		-15.95954 (',	-اند88873	-17,81791	-17.61330 (*,	-17,40869	-17,40869 C.k	-17.20408	-17,20408
2c' Turminal Abren (α ₀)	3,4928		4.0000	4.6904	4,3012	43818	4,4609	4.4772	4.5166	4.5826
2¢' Rend 2 (¢,)	2.09132		2.09132	2.76590	2.76590	151121	2.86175	1,53321	2.86175	2.91548
2c' bend (\alpha_b)	2,09132		2,53321	2,53321	2,53321	2,86175	2.86175	2,86175	2.91548	2 91548
Alman of Augla	ZHC,'H H,C, = C', 1,3-butadiene	$\angle C_sC_sH_s$ $H_sC_s = C_s$ 1,3-butadiene	$AC_{r}C_{s}H_{s}$ $H_{s}C_{s} = C_{s}$ 1,3-butadiene	لار ازار از = حاران ارغ-buradiene	エバ・ア・ア・ C. ₄ = C. ² C, 1,3-cyclopentadiene	∠C,C,C, C,C,⇔C, 1,3-cyclopentadiens	$\angle C_{i}C_{i}C_{i}$ $= C_{i}HC_{i}H_{1}C_{i}(H) = 1.3-\text{evelopentadieno}$	∠د'د'ر'. -H ₂ C' ₂ H'C', هـ C' ₂ H'C' ₂ H ₂ eyelopentene	$\Delta C_{\perp}C_{\mu}C_{\nu}$ $-H_{\perp}C_{\mu}H_{\perp}C_{\mu}HC_{\mu}=C_{\mu}H-C_{\mu}HC_{\mu}=C_{\mu}H$	-`H'.;'H'.;'- 'J';'\

AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple H_2 -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule (C_6H_6) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 C_6H_6 can be considered a linear combination of three ethylene molecules wherein a C-H bond of each CH_2 group of $H_2C=CH_2$ is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule (CH_2CH_2) section. The radius $r_{ethylene2,xy^3}$ (0.85252 a_0) of the $C2sp^3$ shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy $E_{Coulomb}(C_{ethylene}, 2sp^3)$ (-15.95955 eV) of the outer electron of the $C2sp^3$ shell is given by Eq. (14.245). The energy $E(C_{ethylene}, 2sp^3)$ (-15.76868 eV) of the outer electron of the $C2sp^3$ shell 15 is given by Eq. (14.246). $E_T(C=C,2sp^3)$ (-1.13380 eV) (Eq. (14.247), the energy change of each $C2sp^3$ shell with the formation of the C=C-bond MO is given by the difference between $E(C_{ethviene}, 2sp^3)$ and $E(C, 2sp^3)$. C_6H_6 can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two C2sp3 hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each 2sp3 HO of each carbon atom initially has four unpaired electrons. Thus, the 6H atomic orbitals (AOs) of benzene contribute six electrons and the six sp^3 -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the $C2sp^3$ HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two $C2sp^3$ HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination

of one and two diatomic H_2 -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds 5 comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two $C2sp^3$ HOs and 75% of a H_2 -type ellipsoidal MO divided between the $C2sp^3$ HOs:

$$\begin{pmatrix}
3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C) - \text{ethylene-type-bond MO} \\
\rightarrow 6(C=C) - \text{bond MO of benzene}
\end{pmatrix} (15.142)$$

10 The linear combination of each H₂-type ellipsoidal MO with each C2sp³ HO further comprises an excess 25% charge-density contribution per bond from each C2sp³ HO to the C = C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C = C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C = C-bond MO of ethylene (Eqs. (14.242-15.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C = C-bond gives rise to the $C_{benzene} 2sp^3$ HO-shell Coulombic energy $E_{Coulomb} \left(C_{benzene}, 2sp^3 \right)$ given by Eq. (14.245). To meet the equipotential condition of the union of the six $C2sp^3$ HOs, c_2 and c_2 of Eq. (15.42) for the aromatic $c_2 = c_2$ -bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of $e_{Coulomb} \left(C_{benzene}, 2sp^3 \right)$ (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of $e_2 = c_2$ (1.243)):

$$C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$$
 (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4) = 3 electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene, $E_T(C_6H_6,C=C)$, is given by (6)(0.75) times $E_{T+acc}(C=C)$ (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times $E(C,2sp^3)$ (Eq. (14.146)), the initial energy of each $C2sp^3$ HO of each C that forms the C=C bonds of 5 bond order two. Thus, the total energy of the six C=C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6}, C = C\right) = (6)(0.75)E_{T+osc}(C = C) - (6)(3)E(C, 2sp^{3})$$

$$= (6)(0.75)(-66.05796 eV) - 18(-14.63489 eV)$$

$$= -297.26081 eV - (-263.42798 eV)$$

$$= -33.83284 eV$$
(15.144)

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds. $E_{h\nu}$ of an aromatic bond is given by $E_r(H_2)$ (Eqs. (11.212) and (14.486)), the maximum total energy of each H_2 -type MO such that

$$\overline{E}_{osc} = n_1 \left(\overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left(-31.63536831 \ eV \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule (C_6H_6) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by $f_1 = 0.75$ with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{r}(Group) = f_{1} \left(\frac{E(basis\ energies) + E_{\tau}(atom - atom, msp^{3}.AO)}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\epsilon_{o}R^{3}}}} - \frac{1}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{m_{e}}}} + n_{1}\bar{E}_{Kwib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right)$$
(15.146)

The total bond energy of the aromatic group $E_D(Group)$ is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of $c_4 E_{initial}(c_4 AO/HO)$ and $c_5 E_{initial}(c_5 AO/HO)$:

$$E_{D}(Group) = -\left(\int_{1}^{\infty} \left(E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \right) - \left(\int_{1}^{\infty} \left(\frac{C_{1o}C_{2o}e^{2}}{4\pi\epsilon_{o}R^{3}} \right) \right) - \left(\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\epsilon_{o}R^{3}}}}{m_{e}} + n_{1}\bar{E}_{Kwib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right) - \left(c_{4}E_{Initial}(AO/HO) + c_{5}E_{Initial}(c_{5}AO/HO) \right)$$
(15.147)

5 Since there are three electrons per aromatic bond, c_4 is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule (C_6H_6) section. The energy components of V_e , V_p , T, V_m , and E_T are the same as those of the hydrogen carbide radical, except that $E_T(C=C,2sp^3)=-1.13379~eV$ (Eq. (14.247)) is subtracted from $E_T(CH)$ of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding $C2sp^3$ HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with $E_T(atom-atom, msp^3.AO)=-1.13379~eV$.

The total energy of the benzene C-H-bond MO, $E_{T_{brown}}\left(C-H\right)$, given by Eq. (14.467) is the sum of $0.5E_{T}\left(C=C,2sp^{3}\right)$, the energy change of each $C2sp^{3}$ shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), 20 and $E_{T_{benzen}}\left(CH\right)$, the σ MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with $f_{1}=1$ and $E_{T}\left(atom-atom,msp^{3}.AO\right)=\frac{-1.13379\ eV}{2}$. Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to $c_3=1$ in Eq. (15.56) with E_{mos} given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond, $-E_{D_{beaton}}(^{12}CH)$ (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene, $E_T(C_6H_6,C-H)$, given by Eq. (14.494) 10 is

$$E_r(C_6H_6, C-H) = (6)(-E_{D_{brains}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV}$$
 (15.148)

The total bond dissociation energy of benzene, $E_D(C_6H_6)$, given by Eq. (14.495) is the negative

sum of
$$E_T \left(C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and $E_T \left(C_6 H_6, C - H \right)$ (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}\left(C_{6}H_{6}, C = C\right) + E_{T}\left(C_{6}H_{6}, C - H\right)\right)$$

$$= -\left(\left(-33.83284 \ eV\right) + \left(-23.42724 \ eV\right)\right)$$

$$= 57.2601 \ eV$$
(15.149)

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule (C_6H_6) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

al groups of aromatics and hortocyclics.	Group Symbol	2,2	() H.)
Table 15.213. The symbols of functional gr	Functional Graup	CC (aramatic bond)	CH (aromatic)

imental valu							
cs and hertocyclics and exper	CH Grain	1.60061	1.03299	1.09327	1.101 (benzene)	1.22265	0.64537
Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental value	ບ ເຄີຍ ເວີຍ	1.47348	1.31468	1,39140	(399) (benzene)	0.66540	0.89223
Table 15.214. The geometric	Parameter	a (a _o)	$c'(\sigma_b)$	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a_b)	c

S Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. h; is fr_t (ann - ann.nxy², AO).

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	$\begin{pmatrix} d_1 & d_2 \\ (o_a) & (o_a) \end{pmatrix}$		24670	_	175975	
	θ ₂ (Ο)		18 84		28.98	
	e, ①		105.58		45.76	
	(°)		74,42		134.24	
	$\tilde{E}(C2sp^1)$ (eV) Final		-16.90241		-16.90248	
	E(('21p') (eV) Final		-17.09334		-17.09334	
	, re. (a,)		0.79597		0.79597	
	() (g)		0.91771		0.91771	
	Final Total Energy (72.5p)	na i	120,80,27		-133.88327	
	(eV) Bond 4	,	,		,	
	Er (eV) Bond 3	V EXX.00	acanc.	0.000	Armon	
	(eV) Bond 2	A RSMs		-0.85035		
	(eV) Bond 1	-0.85035		-0.15035		
Afom		:		ن ان		
Bond		C H (C.H)	* *)='HC'=C		

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

7400-1012-01-101-01-01-01-01-01-01-01-01-01-01-01	3e	l and mortee
Parameters	C=C Group	CH Group
f_1	0.75	1
n	2	. 1
n_2	0	0
<i>n</i> ₃	0	0
<i>C</i> ₁	0.5	0.75
	0.85252	1
<i>c</i> ₁	1	1
c ₂	0.85252	0.91771
<i>c</i> ₃	0	1
c_4	3	1
<i>c</i> ,	. 0	1
C_{1o}	0.5	0.75
$C_{2\sigma}$	0.85252	1
V_{c} (eV)	-101.12679	-37.10024
V_{p} (eV)	20.69825	13.17125
T(eV)	34.31559	11.58941
$V_m(eV)$	-17.15779	-5.79470
E(AOIHO) (eV)	0	-14.63489
$\Delta E_{H_1MO}(AOIHO)$ (eV)	0	-1.13379
$E_r(AOIHO)$ (eV)	0	-13.50110
$E_{T}(H_{1}MO)$ (eV)	-63.27075	-31.63539
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690
$E_{T}(MO)$ (eV)	-65.53833	-32.20226
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826
E_{κ} (eV)	32.73133	17.43132
$\overline{\widetilde{E}}_{D}$ (eV)	-0.35806	-0.26130
\overline{E}_{Kvih} (eV)	0.19649 [49]	0.35532 Eq. (13.458)
\overline{E}_{asc} (eV)	-0.25982	-0.08364
E_{mag} (eV)	0.14803	0.14803
$E_{_T}(Group)$ (eV)	-49.54347	-32.28590
$E_{ininal}(c_i AOIHO) (eV)$	-14.63489	-14.63489
$E_{initial}(c_s AOIBO) (eV)$	0	-13.59844
$E_{D}(Group)$ (eV)	5.63881	3.90454

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the

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nnenia valu						ڻ ن				_			
	-					ر.		_		_			
3						ຸ ຫ	Atem 2			0.79232			
						ۍ	Yes.			0,79232	•		
The experimental values of	Relative	200000	O.COUCO	(OF casm ma)		Aram 2 Hybridizarioa	Designation	CTable 15.3 A)		7			
	Experimental Total Bond Energy	(ev)	000000	: E. (atom – at	-	G. sankanter	7			-1717218			
l	Tatal Bond To	57.2600E		values [1]. 16, i		Hybridizzaion		(Table 15.3.A)		ξ,			
				xperimental	,	Crantonher Atom			91 CT / CJ	-17.17618			
	H.)			ene and e	-	Temped	Viens	2	7 (696	3			
	C	۰		's of benz	[Doed 1	<u>6</u>		2007	2			
				paranete	.7.6	ij	<u>.</u>		262916 262916 2 6295				
	Name	Benzeno		Table 15.218. The bond angle parameters of benzene and experimental values [1], E_{r} is E_{r} (ann. – ann. mso? AO)	Atoms of Angle				_	(arotnatic)	H.3.77	(risomoso	
	Formula	ĊH,		Table 15							!		

NAPHTHALENE

Naphthalene has the formula $C_{10}H_8$ and comprises a planar molecule with two aromatic rings that share a common C-C group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is (0.75)(4)=3 as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a C-C single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging C-C single bond, and 16 electrons form the eight C-H single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond, c_4 is three times ten, the number of aromatic bonds. Similarly, the aromatic C-H group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten $C2sp^3$ HOs bridged by the C-C single bond, the parameters c_1 , c_2 , and c_3 of Eq. (15.42) are one for the C-C group, 15 C_{10} and C_{11} are 0.5, and c_{12} given by Eq. (15.142) is $c_{12}(C2sp^3HO) = 0.85252$. Otherwise, the solutions of the C-C bond parameters are equivalent to those of the replaced C-H groups with $E(AO/HO) = -14.63489 \, eV$ and $\Delta E_{H_1MO}(AO/HO) = -1.13379 \, eV$ in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with $E_T(atom-atom, msp^3AO) = \frac{-1.13379 \, eV}{2}$.

The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum over the integer multiple of each $E_D(\omega_{PMP})$ of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Comparison Com	nd parameters of naphthaler CH Group 1,60061 1,03299 1,301 (benzene) 1,22265 0.64537
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s" ((°)	02(379		0.55533		-	2000	,	0.1424			
<i>a</i> _	(g)	37.76	1,64070	2000	6.66.9		0.74430		1.18269			
o'	<u>.</u>		38.84	1	38.98		29.66		47.66			
96	€		105.58		45.76		45.19		30,50			
.0	\odot		74.42		134.24		134,81		05 00	2017		
E(C) 50	No.		-16.90248		-16.90248		1661901		(00177)			
(C) (C)	(eV) Final		27.001.14	Control 1	17 09134		, conto	-10.0000		-16.80989		
Γ	(°)		Г	0.19391	0.70107	0.1752		0.80939	ı	0.80739		
	[a]			0.91771		17.16.0		121160		124160		
	Final Total Energy	(4)		-153.88327		-153.18327		153,59983		183 65683		
on, msp .At.).	(eV)			•		٥		•			٥.	
is Er ann - an	E, (eV)	Bond 3		0.0000		05995 0		27100	C#547/0-		0,28345	
sphthalene, Er	(eV)	Bond 2		20000	-0.63033	20000	Croco'n.		0.85035		-0.85035	
parameters of nu	E _r	Bond 1			-0.15035		-0.85035		-0.8.035	-	.0 85035	
trical bond	Atom			1	ـــ ن		<i></i>		ن		•	-
$E_{\rm T}$ is $E_{\rm T}$ (dom = diam, msq. Ar.)	(15.22), the MOId no march Brown				(H.J.) H			(= M(= 1)	*	()=('()')=((C) C'-C'[C']
1	Table Bond			_			٠,	1	م	Ĭ	1	<u>.</u>

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	C = C	СН	C-C
	Group	Group	Group
f_1	0.75	1	1
$n_{\rm l}$	2	1	1
<i>n</i> ₂	0	0	0
n ₃	0	0 -	0
<i>C</i> ₁	0.5	0.75	0.5
<i>C</i> ₂	0.85252	1	1
<i>c</i> ₁	1	1	1
c_{z}	0.85252	0.91771	0.85252
c ₃	0	1	0
<i>c</i> ₄ ·	3	1	2
<i>c</i> ₅	0	1	0
C _{Io}	0.5	0.75	0.5
C ₂₀	0.85252	1	1
$V_{_{u}}$ (eV)	-101.12679	-37.10024	-34.43791
$V_{p}(eV)$	20.69825	13.17125	10.26723
T(eV)	34.31559	11.58941	9.80539
$V_{\rm m}$ (eV)	-17.15779	-5.79470	-4.90270
E(логно) (eV)	0	-14.63489	-14.63489
$\Delta E_{H_2MO}(AOIHO)$ (eV)	0	-1.13379	-1.13379
$E_T(401H0)$ (eV)	0	-13.50110	-13.50110
$E_{T}(H_{1}MO)$ (eV)	-63.27075	-31.63539	-31.63529
$E_{T}(atom-atom, msp^{3}.AO)$ (eV)	-2.26759	-0.56690	-0.56690
$E_{T}(MO)$ (eV)	-65.53833	-32.20226	-32.20226
$\omega \left(10^{15} rad / s\right)$	49.7272	26.4826	23.6343
E_{κ} (eV)	32.73133	17.43132	15.55648
\overline{E}_{D} (eV)	-0.35806	-0.26130	-0.25127
Ē _{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12312 [2]
$\bar{E}_{ax}(eV)$	-0.25982	-0.08364	-0.18971
E_{mag} (eV)	0.14803	0.14803	0.14803
$E_{r}(Group)$ (eV)	-49.54347	-32.28590	-32.39198
E _{initial} (c, AOIHO) (eV).	-14.63489	-14.63489	-14.63489
Enitial (c, AUTHO) (eV)	0	-13.59844	0
$E_{D}^{}(Group)$ (eV)	5.63881	3.90454	3.12220

to the experimental values [2].		
and the energies of Table 15.222 compared	Reficive	
oup composition	Calculated Experimental	
ted using the functional gr	; <u>) </u>	
3. The total bond energies of naphthalene calculat	-	
Table (5,223.		

							۱											
CmC CH)	#53		C-C Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)		g .										
2		-		-	90,74658	90,79143	0,00049	6										
of naphth		Table 15.224. The bond angle parameters of naphthalene and t	l experimen	stal values [1].	E, is Er (aton	experimental values [1]. E_r is E_r (atom – atom, msp ² .40).	<u>.</u>											- 1
(a ₀)	1 1 -	2c' Er	Transports	Atom 1 Hybridization Designation	Ecadorite Alam 1	Atom 2 Hybridizasion Designation	C. Atom (C ₁	U	ڻ'		' ሪ	E_r (eV)	, (e)	(0)	- -	6	ப்
2.65034	1 4	4.5585 -17.17218	7.17218	(A.C.C. olds)	-17.17218	34	0.79232	0,79232	-	-	-	0.79232	-1.85836		-	119.40		(nap
T	1	\vdash	-			-				 				=	119.40	סניסבו	g	
2036	[_4	262036 4.5585 -17	7.17218	34	17,17218	7.	0.79232	0.79232	-	-	-	0.79232	-1.85836			120.19	9	E &
\vdash		-	-								 : ·				120.19	119.91		₽. ©

TOLUENE

Toluene has the formula C_7H_8 and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a CH_3 functional group and a C-C functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a C-C functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the 2s and 2p AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, E(AO/HO) and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.41) are -15.35946~eV (Eq. (14.155)) and $\frac{-1.13379~eV}{2}$, respectively.

To meet the equipotential condition of the union of the aromatic and methyl $C2sp^3$ HOs of the C-C single bond, the parameters c_1 , C_2 , and C_{2o} of Eq. (15.42) are one for the C-C group, C_{1o} and C_1 are 0.5, and c_2 given by Eq. (13.430) is $c_2(C2sp^3HO) = 0.91771$. To match the energies of the functional groups, $E_T(atom-atom,msp^3.AO)$ of the C-C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is $-1.13379 \, eV$ which is the same energy per $C2sp^3$ HO as that of the replaced C-H group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

	0 3	ت	5
	6	 ©	79.89
	E(C247)	(cV) Final	-15.20178
	E. (C24")	(eV) (eV) Final Final	-15,39265
	7.	(°)	Cotago
:	1	ો જે	
,	Einel Total	Energy	(eV)
	(Or eds)	(eV)	Bond 4
	E_{ij} is E_{ij} (atom - atom, inq^{3} AO).		Bond 3
1.27295	oluene. Er is L	E.	Bond 2
1,47774	d parameters of 1	Er	(ev) Bond 1
1 1 !	retrical bon	Atom	
1.22265	escent redi		
66540	di Cu		
. 06		D. LIIC IM	
h.c (a ₀)	-	Table 15.2. Bond	
		-	

Table 15,226. The premuetrical bond parameters of folluene and experimental values [I].

Parameter C=C Group Group Group Group

o (a,) 1.41348 1.60061 2.06004 1.64920

o'(4,) 1.31468 1.03299 (.43528 1.04856

C=C CH (3) C-C C-H (CH₃)

Table 15,225. The symbols of functional groups of toluene.

Functional Group

C = C

CC (aromatic bond)

CH (aromatic)

C = C

CH (i) c aromatic bond)

C = C

CH (i) c aromatic bond)

CH, group

1,10974

1,51904

1.09327

1,39140

c' (a_e)
Bond Length
2c' (A)
Exp. Bond
Length
(A)

1.524 (toluene)

1.11 (avg.) (loluene)

1.399 (toluene)

(a,)	0.15511	21117	215.30	_	0.55533		-	0.25779		0.37901				
(°)	1,20367		1.24678		0.75935			1.68807	1	1,81430				
·C	1,2,7	2	38.84		80 45	<u> </u>		34.97		75.37	-			
		11.10	105.58		ì	45.76		106.62		:	118.04			
, ©		61.67	74.42			134.24		73.38	-		61:56			
E(C247') (eV)		-15.20178	arway.	10.302.0	_	-16.90248		16 20178			-16.90247			
(cv)		-15,39265		.17,09334		-17,09334			core.	1	-17,09334			
'J <u>'S</u>		701990	0.000	0,79597		19207.0			0.88392		Toyot o			
, (a)			0.91771	17719.0		0.91771			17716.0			0.916.0		
Final Total Energy	,dr.C	(ev)	.152,18259	153 88327		72588 127			95281.221			. (53.88323		
E,	Bond 4		•		0	•	,		_	•		۰		
Er Er	Bond 3		0		0.56690		-0.16690		:	.		0.\$5035		
luene. Er is E	(ev)		,	,	-0.85035		-0.83035			0		510530	200	
parameters of to	ر ا	Bond 1		-0,36690	-0.85035		-0.85035			-0.36690			-0.56690	
Atom Atom	_		†	۔۔۔ 'ن	1		٠,	ڻ	+	- ن -			ت ن*	
Table 15.227. The MO to HO interacting geometrical bond parameters of tolurene. E_1 is E_2 , farming the E_2 and E_3 and E_4 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 and E_7 a				(7.7)	$C = H \left(\mathbf{t}_{i,0} \mathbf{n}_{j} \right)$	C-H (C,H)	JH JH JH JH JH JH JH JH JH JH JH JH JH J		C=(H,C,)C,=C		("-("H")	(3		
Table 1]	١	C- H	£ 1.	j si	<u>`</u>	-	11			

Table 15.228. The energy parameters (eV) of functional groups of toluene.

Table 15.228. The energy paramet	3 <i>e</i>	CH (i)	C-C	CH ₃
Parameters	C=C Group	Group	Group	Group
f_1	0.75	1		
$n_{\rm l}$	2	1	1	3
n_2	0	0	0	2
n ₃	0	0	0	0
C_1	0.5	0.75	0.5	0.75
C_2	0.85252	1	1	1
c_{i}	1	1	ı	1
<i>c</i> ₂	0.85252	0.91771	0.91771	0.91771
<i>c</i> ₃	0	1	0	0
C ₄	3	1	2	1
$c_{\rm s}$	0	1	0	3
C_{1o}	0.5	0.75	0.5	0.75
C ₂₀	0.85252	1	1	1
V, (eV)	-101.12679	-37.10024	-29.95792	-107.32728
$V_{p}(eV)$	20.69825	13.17125	9.47952	38.92728
T(eV)	34.31559	11.58941	7.27120	32.53914
$V_m(eV)$	-17.15779	-5.79470	-3.63560	-16.26957
. E(логно) (eV)	0 .	-14.63489	-15.35946	-15.56407
$\Delta E_{H_1MO}(M) (eV)$	0	-1.13379	-0.56690	0
$E_r(AOIHO) (eV)$	0	-13.50110	-14:79257	-15.56407
$E_{T}(H_{2}MO)$ (eV)	-63.27075	-31.63539	-31.63537	-67.69451
$E_{\gamma}(atom-atom,msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0
$E_{r}(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-67.69450
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	16.2731	24.9286
E_{κ} (eV)	32.73133	17.43132	10.71127	16.40846
$\bar{E}_{_D}$ (eV)	-0.35806	-0.26130	-0.21217	-0.25352
\overline{E}_{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
\overline{E}_{osc} (eV)	-0.25982	-0.08364	-0.13747	-0.22757
E_{mag} (eV)	0.14803	0.14803	0.14803	0.14803
$E_{r}(Group)$ (eV)	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(\epsilon_{4}$ ΑΟΙ ΗΟ $)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{tintial}(c_s A(T)HO) (eV)$	0	-13.59844	0	-13.59844
$E_{D}(cirup) (eV)$	5.63881	3.90454	3.63685	12.49186

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unctional group co	Crew	-		le parameters of toluene and experimental values [1] IF is IF [11 17 try 13	Atom !	Hybridization Designation	(Table (5.3.A)		ች	
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CHLOROBENZENES

Chlorobenzenes have the formula $C_6H_{6-m}Cl_m$ and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a C-Cl functional group. The aromatic C=C and C-H functional groups are equivalent to those 5 of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to E_{asc} . Two types of C-Cl functional groups can be identified based on symmetry that determine the parameter R in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of Cl for H. P-dichlorobenzene is representative of the bonding with R=a. 1,2,3-trichlorbenzene is the particular case wherein is R=b. Also, beyond the binding of three chlorides E_{mag} is subtracted for each additional Cl due to the formation of an unpaired electrons on each C-Cl bond.

The bond between the chlorine and aromatic ring comprises two C - Cl functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the 2s and 2p AOs of each C hybridize to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between the C2sp³ HO and Cl AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. As in the case of alkyl chlorides, c_2 of Eq. (15.52) for each C - Cl-bond MO is one, and the energy matching condition is determined by the C_2 parameter given by Eq. (15.111) which is $C_2(C2sp³HO to Cl) = 0.81317$. To match energies within the MO that bridges the chlorine AO and aromatic carbon C2sp³ HO, E(AO/HO) and $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) are -14.63489 eV and -2.99216 eV, 25 respectively. The latter matches twice that of the replaced C - H-bond MO plus $E_T(atom-atom, msp³.AO)$. To match the energies of the functional groups, $E_T(atom-atom, msp³.AO)$ of the C - Cl-bond MO in Eq. (15.53) due to the charge donation from the C and Cl atoms to the MO is -0.72457 eV (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each $E_D(G_{POUP})$ of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(G_{POUP})$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Cl-C (Cl to aromatic bond)	C-Cl (a)
Cl-C (Cl to aromatic bond of 1,3,5-trichlorbenzene)	C – Cl (b)

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	Aloin	(eV)	(eV)	(eV) Bond 3	E ₇ (eV)	Final Total Energy ('24p'	(°)	(a)	(eV)	E(C24p³)	(e)	© _6	ه. ۞	2. (2)	<i>a a</i>
: (a)						ŝ			i	Final			;	(-
-H (C,H)	.:	-0.85035	-0.85035	-0.5690	. 0	-153,88327	0.91771	0.79597	-17.09334	-16 90248	74.47	1000			
C=HC;=C	رځ	-0.8503.5	-0.85035	-0.56690		-153.88327	0.91771	0.79397	-17.09334	-16.90248	114.74	XC 2x			6/5/70
												1	96.96	0.73933	ננפטט
C=\C'-C'	Ç	-0.36229	-0.85035	-0.85035	0	-153,67867	0.91771	0.80561	-16.88873	-16.697B6	73,32	106,68	31.67	1.87911	0.23129
$C = \int_{3} C_{n} - CI$?	-0.36229		0	0		1.05158	0.19582	15.18804		\$2.92	97.08	J722	1 75824	
(= (')\(: = (')															
$(C_k \text{ bound to } H \text{ or } C_k)$,;;	-0.36229	-0.85035	-0.85015	•	-153.67867	0.91771	0.80561	-16.88873	-16.69716	134.65	\$5.35	59,47	0.74854	0.36674

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		o (o) or runotronu	groups of chilotopetizeties.

Parameters	C = C	CH (i)	C-Cl (a)	C-CI (b)
	Group	Group	Group	Group
f_1	0.75	1		
η	2	1	1	1
n _z	0 .	0	0	0
<i>n</i> ₃	0	0	0	0
<i>C</i> ₁	0.5	0.75	0.5	0.5
C ₂	0.85252	1	0.81317	0.81317
<u>c₁</u>	1]	1	1
<i>c</i> ₂	0.85252	0.91771	1	1
<i>c</i> ₂ .	0	1	. 0	0
<i>c</i> ₄	3	J	2	2
<i>c</i> ₅	0	1	0	0
C ₁₀	0.5	0.75	0.5	0.5
C _{2n}	0.85252	1	0.81317	0.81317
V _e (eV)	-101.12679	-37.10024	-31.85648	-31.85648
V, (eV)	20.69825	13.17125	8.25686	8.25686
T (eV)	34.31559	11.58941	7.21391	7.21391
V _m (eV)	-17.15779	-5.79470	-3.60695	-3.60695
E(логно) (e)')	0	-14.63489	-14.63489	-14:63489
$\Delta E_{H_2MO}(MOIHO)$ (eV)	0	-1.13379	-2.99216	-2.99216
$E_{\gamma}(AOIHO)$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_{\gamma}(H,MO)$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_{\tau}(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_{\tau}(MO)$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
ω (1013 rad / s)	49.7272	26.4826	8.03459	14.7956
E_{K} (eV)	32.73133	17.43132	5.28851	9.73870
\bar{E}_n (eV)	-0.35806	-0.26130	-0.14722	-0.19978
$\overline{E}_{K_{P}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059
$\tilde{E}_{ox}(eV)$	-0.25982	-0.08364	-0.10693	-0.15949
E_{meg} (eV)	0.14803	0.14803	0.14803	0.14803
$E_{r}(Group)$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
E _{inited} (c, AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-14.63489
E _{Initial} (c, AOTHO) (eV)	0	-13.59844	0	0
$E_D(Grap)$ (eV)	5.63881	3.90454	3.19709	3.24965

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16,611	120.19	Cal. θ
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of the $E_n(\omega_{mp})$ (eV) values based on composition is given by (15.58). Table 15.233. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [2]. The magnetic energy E_{neg} that is subtracted from the weighted sum

C=C

CH (i)

Group (a)

C~(1 (b) Group

PHENOL

Phenol has the formula C_6H_6O and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an OH functional group and a C-O functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a C-O functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the 2s and 2p AOs of each C hybridize to form a single $2sp^3$ 10 shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and O AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the O AO has an energy of $E(O) = -13.61806 \, eV$. To meet the equipotential condition of the union of the C-O H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.52) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(arylC2sp^{3}HO \ to \ O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \ eV}{-14.63489 \ eV}(0.85252)$$

$$= 0.79329$$
(15.150)

 $E_T(atom-atom, msp^3.AO)$ of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is $-1.49608 \, eV$. It is based on the energy 20 match between the OH group and the $C2sp^3$ HO of an aryl group and is given by the linear combination of $-0.92918 \, eV$ (Eq. (14.513)) and $-1.13379 \, eV$ (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each $E_D(armp)$ of Table 15.240

corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Aryl C-O	C-O (a)
OH group	· OH

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

14010 13.230.	ne geometrien oc	na parameters or p		indiated [1]
Parameter	C = C Group	CH (i) Group	C−O (a) Group	<i>OH</i> Group
$a(a_0)$	1.47348	1.60061	1.68220	1.26430
$c'(a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c'(A)$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length (Å)	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b,c(a_0)$	0.66540	1.22265	1.07126	0.86925
е	0.89223	0.64537	0.77101	0.72615

Bond	Atom	1:3	£3	E_{f}	43	Final Total	, and a	ren'	E (C'24)	$E(C2sp^2)$	eō.	θ	θ	4	
		(cV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy ('2 <i>sp'</i> (eV)	(a,)		(eV) Final	୍ଞ ବ	()	(°)	(°)	(a,)	
(,-H (C'H)	۲,	-0.×5033	-0.85033	-0.36690	0	-153.88327	11,160	0.79597	-17.09334	-16,90248	74,42	105.58	31.14	1.24578	
$\left(C_{\star}^{=}\right)^{2}C_{\bullet}D-H$	0	-0.74804	0	0	0		1.00000	0,87363	-15.57379		115.79	64.21	64.82	0.53799	
$C_{\star}^{\star} = \begin{pmatrix} C_{\star} - OH \end{pmatrix}$.,	-0.74XO-	-11.X5035	-U.N.JOJS	0	-134,06442	0,91771	0.78762	-17.27448	-17,08362	100.00	80.00	46.39	1.16026	, ,
(C, =) (C-OH	. 0	1044/10-	e	ć	O	-	1 00000	0.87363	15.57379		16,501	73,49	51.43	1.04871	
(;=) (;=)	<i>(</i> ;	-0.7480-4	-0.85035	-0.8503 <i>\$</i>	0	-134.06442	0.91771	0.78762	-17.2744Ж	-17,08362	133.48	46.12	58.35	0.76870	
(=(H)c') C'OH	·	-41.W5035	-0.850JS	-0.56690	ū	-153,88327	0.91771	0.79597	-[7.09JJ4	-16.90248	134,24	45.76	36.85	0.75935	

Table 15.240. The energy parameters (eV) of functional groups of phenol.

Table 15.240. The energy paramet	ers (eV) of funct			077
Parameters	C=C Group	CH (i) Group	C – O (a) Group	OH Group
f_1	0.75	1		
n	2	1	1	1
n_2	0	0	0	0
n_3	0	0	0	0
C_1	0.5	0.75	0.5	0.75
<i>C</i> ,	0.85252	1	1	1
<i>c</i> ₁	1	1	1	0.75
<i>c</i> ,	0.85252	0.91771	0.79329	1
<i>c</i> ,	0	1	0	1
C ₄	3	1	2]
c,	0	1	0	1
C ₁₀	0.5	0.75	0.5	0.75
C ₂₀	0.85252	· 1	1 .	1
V (eV)	-101.12679	-37.10024	-34.04658	-40.92709
$V_{p}(eV)$	20.69825	13.17125	10.49024	14.81988
T(eV)	34.31559	11.58941	10.11966	16.18567
V_n (eV)	-17.15779	-5.79470	-5.05983	-8.09284
E(логно) (eV)	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}(AOIHO)$ (eV)	0	-1.13379	-1.49608	0
$E_{T}(AOIHO)$ (eV)	0	-13.50110	-13.13881	-13.6181
$E_{r}(H,MO)$ (eV)	-63.27075	-31.63539	-31.63532	-31.63247
$E_{\tau}(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.49608	0
$E_r(M)$ (eV)	-65.53833	-32.20226	-33,13145	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	13.3984	44.1776
E_{κ} (eV)	32.73133	17.43132	8.81907	29.07844
\bar{E}_{p} (eV)	-0.35806	-0.26130	-0.19465 ·	-0.33749
\overline{E}_{Kvib} (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
$ar{E}_{ m urc}$ (eV)	-0.25982	-0.08364	-0.13061	-0.10594
E_{mag} (eV)	0.14803	0.14803	0.14803	0.11441
$E_{\tau}(c_{roup}) (eV)$	-49.54347	-32.28590	-33.26206	-31.74130
Entrat (c. AOTHO) (eV)	-14.63489	-14.63489	-14.63489	-13.6181
E _{imsal} (c, логно) (eV)	0	-13.59844	0	-13.59844
$E_{\scriptscriptstyle D}$ (Group) (eV)	5.63881	3.90454	3.99228	4.41035

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(~ - !		-1.85826 (eV)					C; C; c4 c4	C; C; c, c, c,	C; C; c4 c4	Atom 2 C ₁ C ₂ C ₃ C ₄ C ₅ C ₅ C ₇ Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Accent Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Access Ac	Alam 1	Alam 1	Alam 1	Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asian Asia	

ANILNE

Aniline and methyl aniline have the formula C_6H_7N and C_7H_9N , respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an NH_2 functional group and a C-N functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The C-C and CH_3 functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino (NH_2) functional group was solved using the procedure given in the Dihydrogen Nitride (NH_2) section. Using the results of Eqs. (13.245-13.368), the aryl amino 10 parameters in Eq. (15.51) are $n_1 = 2$, $C_1 = 0.75$, $C_2 = 0.93613$ (Eqs. (13.248-13.249)), $C_{1o} = 1.5$, and $c_1 = 0.75$. In the determination of the hybridization factor c_2 of Eq. (15.52) for the N-H-bond MO of aryl amines, the $C2sp^3$ HO of the $C-NH_2$ -bond MO has an energy of $E(C,2sp^3) = -15.76868$ eV (Eq. (15.18) corresponding to s=2 in Eqs. (15.18-15.20), and the N AO has an energy of E(N) = -14.53414 eV. To meet the equipotential condition of the union of the N-H H_2 -type-ellipsoidal-MO with the $C2sp^3$ HO, the hybridization factor c_2 given by Eq. (15.68) is

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171$$
 (15.151)

The bond between the amino and aromatic ring comprises a C-N functional group that is the same as that of 2° amines (methylene) except that the energies corresponding 20 to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the 2s and 2p AOs of each C hybridize to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and N AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the C-O group of phenol. In anilines, the aromatic $C2sp^3$ HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of $E(C,2sp^3) = -14.63489 \, eV$ (Eq. (15.25)) and the N AO has an energy

of $E(N) = -14.53414 \, eV$. To meet the equipotential condition of the union of the C-O H_2 -type-ellipsoidal-MO with these orbitals, the hybridization factor c_2 of Eq. (15.51) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252)$$

$$= 0.84665$$
(15.152)

5 $E_T(atom-atom, msp^3.AO)$ of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is -1.13379~eV (Eq. (14.247)). It is based on the energy match between the NH_2 group and the $C2sp^3$ HO of the aryl group and is twice that of the

aryl C-H group that it replaces.

- The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in Table 15.247 was calculated as the sum over the integer multiple of each E_D (Group) of Table
- 13.247 was calculated as the sum over the integer multiple of each E_{D} (Group) of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

20 Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	3" C=C
CH (aromatic)	CH (i)
Aryl C-N	C-N (a)
NH₂ group	NH_2
$C_a - C_b$ (CH ₃ to aromatic bond)	C-C (a)
CH ₃ group	$C-H(CH_3)$

5	of and methyl-substituted antitues and experimental values 11	ments of aniline and	methyl-substituted an	Hines and experimen	at values 11.		
	reconcincal bong par	CH CD	C-N (B)	NH3	(a) (b) (c) (d)	('-'H (CH')	
Parcineter	<i>ن</i> و	Group	Group	Group	Graup	Group	
T	Croup.	190091	1.81158	1.24428	2.06004	1.64920	
T	2000	1,03299	1.34595	0.94134	1,43528	1.04856	
(a)	1,31408					1,000	
Bond Length	1,39140	1,09327	1,42449	0.99627	1,51904	1.10217	
Exp. Bond Length	1,397 evg. (phenal)	1.084 (phenol)	1.431 (aniline)	0.908 (miline)	1.524 (toluene)	1.11 (avg.) (roluene)	
				2000	ACCEA :	1,27295	
_	0.66540	1,22265	1,21254	0.615.0	1,7,7,7		
7. (**)			79777	0.75653	0.69673	0.63380	
	0.89223	0.04537	,,,,,				

1	mainten han	d corremeters of a	aniline and meth	there of aniline and methyl-substituted annines. Zr 13 Lr	(INC). Ar 13 4.		,					ľ	٩	`	9
Table 15,245. The MO to HO intercept geometrical conditions	income non			-	"	Final Total				E(C2sp2)		5	5 ' ;	 - (r (
Bond	Atom	₽ (§)	(e.y.	(eV)	Band 4	Energy (729)	(a)	હ	S Final	Final Final	• •	 ©	€	(ф)	(%)
		n none	7 71100	2000		(6)	1			ar Eva y	14.63	105.58	71.74	1,24678	0.21379
	.	0.00036	0.75/05	06995-0-	•	-155,KK32K	17719.0	0 79597	.17.09134	יומיקיים!					0 15511
C-H (C.H)	-					98281 531-	12716.0	O.KB392	-15.39265	-15.2017R	70.89	101.11	43.13	/wmr	
C-H (C,H,)		-0.56690	0	-	,			1	27,007,71		121.74	SR.26	67.43	0.47634	0,46500
(C) C. NH - H	2	OK995'U*	6		c		0.93084	0,88392	mazere).						
(*)	ļ.		10700	Susa a.	6	1(53,53).	17716.0	0.70597	M200,71.	-16,9024R	AY SE	15,18	10'1+	1.36696	0.02101
(',=) (', - NH;	ا •	Marketo.	egneral.								1	9:	66.43	124359	0.09736
$y_{ij} = y_{ij} \left(\frac{1}{2}, \frac{1}{2} \right)$	>	0.56690	•		c		0.930#4	0 88392	-15.39263		10 K	200			
(c,=)(,=mn;	:								Sylut si	15.00.78	75.38	106.63	34.97	1,68207	0.25279
	ن 	-0.56690	٥.	-	•	-152.18259	0,9177	O.KN392	CH246.61-						
(, -),	.	-						E STORY OF	P2200 E1	16.90247	61.36	118.44	72,82	1.81430	0.37901
$\begin{pmatrix} c & c \\ c & d \end{pmatrix}$	ڻ 	4156690	-0,85035	-0.85035	e	-153,88328	0,91711	d. (959)							
,	ن							1	7000	IK onzáš	134.24	45.76	58.98	25957.0	0.55333
(= (H,N)C.	: •ی • ——	-0.45(135	-0,11503.5	-0.56690	o	153.8337	0,9177	0.79397							
# 5/ 5 # 5/ 5 # 5/ 5 # 5/ 5 # 5/ 5 # 5/ 5 # 5/ 5 # 5/ 5 # 5/ 5/ 5/ 5/ 5/ 5/ 5/ 5/ 5/ 5/ 5/ 5/ 5/	ڻ 														
		-	-												

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	C=C Group	CH (i) Group	C - N (a) Group	NH ₁ Group	C-C (a) Group	CH ₃
f_1	0.75	1		Group		Group
n	2	1	1	2	1	3
n_2	0	0	0	0	0	2
n ₃	0	0	0	1	0	0
, C,	0.5	0.75	0.5	0.75	0.5	0.75
<i>C</i> ₂	0.85252	1	1	0.93613	1	1
C ₁	1	1	1	0.75	1	1
C ₂	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
<i>c</i> ₃	0	1	0	0	0	0
c_4	3	1	2	1	2	1
c_{5}	0	. 1	0	2	0	3
C _{Io}	0.5	0.75	0.5	1.5	0.5	0.75
C ₂₀	0.85252	1	1	1	1	1
V. (eV)	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
V_{ρ} (eV)	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
T (eV)	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
$V_{m}(eV)$	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
E(MOIHO) (eV)	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{H_2MO}(\lambda O) (eV)$	0	-1.13379	-1.13379	0	-0.56690	0
$E_{I}(AOIHO)$ (eV)	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
E(n, 10140) (eV)	. 0	0	0	-14.53414	0	0
$E_{\gamma}(H,MI)$ (eV)	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_{\tau}(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_{\tau}(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
E_{κ} (eV)	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
\bar{E}_{D} (eV)	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0.25352
$ar{E}_{_{KVL}}$ (eV)	0.19649 [49]	0.35532 · Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
\widetilde{E}_{aw} (eV)	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
$E_{ming}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\tau}(Group)$ (eV)	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
E _{lantol} (c, AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
Einthial (c, ACTHO) (eV)	0	-13.59844	0	-13.59844	0	-13.59844
$E_D(Group)$ (eV)	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186

Formula	Name		ر ار	C=C (.H (!)		C-N (a) Group	Orano	Croup	CH,	Total Bond		Total Bond Energy		Rulative Error						
S,H,O	Andline		-		5		 -	•	ď	64 433		A11.4	1	10001						
ないこと	2-methybrilling		•		-	_	_		-	76.6234		76.643		20025						
C,T,O	3-mulhylaniline		•		7	_		_	_	76.62		76.661		0000						
N,H,D	4-methylamiline		9		•	-	_	-	-	76,6234		76.654		0,00040						•
Table I.	Table 15.248. The bond angle parameters of aniline and methyl-si	gle paramet	ers of ani	line and 11	rethyl-subst	inted anilines and	l experimenta	substituted anilines and experimental values [1]. E_r is E_r (atom – atom, msp ² .AO)	s E _r (atom – an	om,msp2.AO).										
	Aktus of Angle	2¢' Imad I (a,)	2c' fred 2 (u ₀)	2c° Torrainal Attorno	Erne Agenta	Atom I Hybridization Designation	Erneman. Aum 2	Atom 2 Hybridization Designation	C. S. Alexandra	C; Alen 2	Ů.	ť	٠,	٧.	E, (eV)	9, ①	6 C	0, ©	(j. (c.	Exp. <i>θ</i>
Ì				(0)		(Table 15,3.A)		(Table 15.3.A)										_		
	ZCCX*	W6257	2 62936	4 55K5 - 17.172	-f7.17218	76	81271.71-	æ	0.79232	0.79232	-	_	-	0.79232	-1,83836			\vdash	120.19	120 [50-52]
	Art. H (aromatic)																120.19		16.91	120 (50-52) (benzene)
	HNH7	нугих і	1 RK25CK	3,1559	1 RH26N 3,1559 -14,53414	z	×	×	0,93613 Eq.(13,248))	-	-	_	67.0	1.06823				T	13.89	113.9 (aniline)
	CHING.	RAZKK!	2,69100	4.033	LXXZ6H Z.69190 4.0332 -14.53414	z	.13,95955	6	0.84665	0.86284	51.0	_	0.75	1.01912	o		r		122.70	

ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an NO_2 functional group and a C-N functional group. Examples include nitrobenzene, nitrophenol, and nitroanilne with formulas $C_6H_5NO_2$, $C_6H_5NO_3$, and $C_6H_6N_2O_2$, respectively. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH and C-O functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The NH_2 and C-N functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond onergies of the nitroanilines given in Table 15.252 are due to differences in the E_{axc} term. For simplicity and since the differences are small, the E_{axc} terms for nitroanilines were taken as the same.

The NO_2 group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a C-N functional group that is the same as 15 that of nitroalkanes given in the corresponding section except that $E_T(atom-atom,msp^3.AO)$ is -0.72457~eV, one half of that of the C-N-bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the $C2sp^3$ HO magnetic energy E_{mag} that is subtracted from the weighted sum of the $E_D(Group)$ (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

oups of aryl nitto compounds. Group Symbol	3.6	つ (1) (1)	C-N (a)	C-N (b)	C-0 (a)	ON	, , , , , , , , , , , , , , , , , , ,	OH.	
Table 15.249. The symbols of functional groups of aryl nitro compounce. Group Symbol	r uncuoliai Otoak	CC (aromatic bond)	CH (aromatic)	Aryl C-N (aniline)	Aryl C-N (nitro)	Aryl C-0	NO ₂ group	NH, group	OH group

	HO	Group	1 26430	20107:1	0 91808			0.971651			0.956	(phenol)		0.86925	1	0.72615		
	NH	Group	24400	1.24420	0.04124	1.741.7		70000	0.59021	-	866 0	(aniline)	,	0.81370	0.010.0	0.75653		
Ξ		10 S	dnoiD	1.33221		1.15421			1.22157		1.224	(nitromethane	^	00000	0.50020	0.86439	7.000.0	
	hand narameters of aryl nitro compounds and experimental values [1]	C-0 (a)	Group	1 68220	2001	1.29700			1.37268			1.364	(ionand)		1.07126	10.00	0.77101	
,	mpounds and ex	C-N (b)	Group	1,0770	1.91174	1 40639	10000		1.48846					-	1 39079		0.71104	
	s of aryl nitro co	C-N (a)	Group		1.81158	1 24505	1.34373		1.42449		-	1.431	(aniline)		1 01054	1.21234	0 74797	0.1157
	I bond parameter	(CH (C)	Group		1.60061		1.03299		1.09327			1.084	(phenol)	, ,		1.22265	20110	0.64557
	T	Table 15.250. The geometrical	ر ا ا	Croup	1 47348	21	1.31468		1 20140	04166.1		1 207 946	(L.)7, av6.	(paraid)		0.66540		0.89223
On Broup		Table 15.250.	Parameter		(")"	(00)	$c'(a_i)$		Bond	100 100 100 100 100 100 100 100 100 100	2c' (A)	Exp. Bond	Length	(F)		7 (0)	(0) 250	

1		I													
	— — A tom	(eV) Bond }	E _r (eV) Bond 2	E ₇ (eV)	E, (eV)	Final Total Energy C2rp	(a)	7 8	fa(C.149)	$E(C2sp^2)$. 0	ø_ <u> </u>	6,5	d,	4
C-H (C,H)	ارز	-0.83035	20,8635	0.66600		(e.y.			ring	Final	; 	<u> </u>	=	(%)	(%)
(C, x) C,0-H	5	70.75		O'CHAPTON O	9	-153.88527	0.91771	0.79597	17,09334	-16.90248	74,43	105.58	38.86	1.24671	0,21379
(, ')	<u>:</u>	-ti. /4x04	•	e	c		1.00000	0.87363	OCETA.81-		113.79	2.38	64.82	0.53799	0.52000
(C _k =) C _k - OH	.	-0.74804	-0.83035	-0.85035	c	-154,06442	0.91771	0.78762	-17.27448	-17.08362	50 001	8	!		
(C, =) C, -OH	0	-0.74H04	0	o	0		1.00000	192263				m'a	(F 0)	22031.1	0.13674
HÓ	"	-0 74RM	360340						9555		106.51	73.49	51.43	1,04871	0.24829
, Ja.);;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;	•		Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of the Constant of th	47.45065	۵	-154.06442	17716.0	0.78762	-17,27448	-17.08362	133.88	46.12	58.55	0.76870	80%542.0
$C = (H_1N)C_{\frac{N}{2}}$	ပံ : 							_							
(=(H)C,) C,0H		-0.13035	-0.85035	-0.56690	۰	-153.KR327	0.91771	0,79597	-17.09334	-16.90248	134.24	. 92.53	ac as		
$C = \left(H(C_x)\right) C_x = C$	ر•													C C C C C C C C C C C C C C C C C C C	0.55533
$C_s = C_s NH - H$	2	-0.56690	c	0	5		70000								
C, B C, -NH;	ن	0.56600	-0.83033	20880			0.93024	0.188392	15.39263		121.74	58,26	67.49	0,47634	0.46500
(*) (- NH	, - -			Concur.	=	-153.84324	1221670	0.79597	-17.09334	-16,90248	\$R.49	15.19	41.01	1.36696	0.02101
(4)	*	-0.566m	0	0	c		0.93084	0.44392	-15.39265		26.32	R3.G8	46,43	1 24850	7,500
(= \ (; -(,H,	ن'	-0.36690	5	U	c	-152.18259	0.91771	0.88392	-15,39263	-15 20171	e F	1			0000
(=) (; -(; H;	ئ	-0.56690	-0.83035	-0.K\$03.5	0	-153 RH328	0.91771	0.79597	17003.5		ure;	10.00	34.97	1.63807	0.15279
W(O) = 0	o	41.929.1x	•	10		1			************	10.30247	61.56	¥.	28.27	1,11430	0.37901
(3)	2	0.9291X	4192918	0.34229	c	$\frac{1}{ }$	0.00000	0.86339	-15.75493		135.25	44.75	66.05	0.54089	0.61::::
C= 1 C, - NO;	ئ:	03622U	-0.11503.5	-0.85655	-		10000	0.79416	-17.046-10		132.36	47.64	17.79	0.61640	0.53781
C=), C, -NO,	2	-0.9291K	#1959 CF	urear o	, ,	193.04801	111111111111111111111111111111111111111	0.80361	-16.RRK73	-16.69786	72.49	107.51	33.53	1,64115	0.24236
)=./(\(\superpressure \)=.	i	A 46330	2.070.0		>		0.93084	0.73H16	-17.04640		65.17	108.47	32.9x	1,65923	0.252%
	,		CCUCA.	-0.85035	0	-153.67867	17716.0	0 x0561	-16,8RR73	-16.69786	177.00	153		+	T

Table 15.251. The MO to HO intercept geometrical bond parameters of any intro compounds. E_T is E_T (atom - atom, map² AO).

Bond

Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Table 15.252. The energy parame	ters (eV) of fun	ctional groups of	of aryl nitro con	npounds.				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Parameters				, , ,		1 -	, .	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	f_1	0.75	1	<u> </u>			0.00	Group	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		2	1	1	. 1	1	2	1 2	
$ \begin{array}{c} r_{3} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{4} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{5} $	n ₂	0	0	0	0	0	0		+
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	n,	0	0	0	0	0	0		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	G	0.5	0.75	0.5	0.5	0.5	0.5		-
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C,	0.85252	1 .	1	1	1	1		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	I	1	1	1	1	1		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	c,	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	c ₃	0	1	0	0	0			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C ₄	3	1	2	2	2		·	
$ \begin{array}{c} C_{\rm in} & 0.5 & 0.75 & 0.5 & 0.5 & 0.5 & 0.5 & 0.5 \\ C_{2\nu} & 0.85252 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ V_{\nu}(eV) & -101.12679 & -37.10024 & -32.76465 & -31.36351 & -34.04658 & -106.90919 & -78.97795 & -40.92709 \\ V_{\nu}(eV) & 20.69825 & 13.17125 & 10.10870 & 9.67426 & 10.49024 & 23.57588 & 28.90735 & 14.81988 \\ T(eV) & 34.31559 & 11.58941 & 9.04312 & 7.92833 & 10.11966 & 40.12475 & 31.73641 & 16.18567 \\ W_{\mu}(eV) & -17.15779 & -5.79470 & -4.52156 & -3.96416 & 5.05983 & -20.06238 & -15.86820 & -8.09284 \\ E[aumo](eV) & 0 & -14.63489 & -14.63489 & -14.63489 & 0 & -14.53414 & -13.6181 \\ \Delta E_{\mu_1\mu_2}(aumo)(eV) & 0 & -1.13379 & -1.13379 & -0.72457 & -1.49608 & 0 & 0 & 0 \\ E_{\mu}(aumo)(eV) & 0 & -13.50110 & -13.50110 & -13.91032 & -63.27093 & -48.73654 & -31.63541 \\ E[a_{\mu}aumo](eV) & 0 & 0 & 0 & 0 & 0 & 0 & -14.53414 & -13.6181 \\ E[a_{\mu}aumo](eV) & 0 & -13.50110 & -13.50110 & -13.91032 & -63.27093 & -48.73654 & -31.63547 \\ E_{\mu}(aumo)(eV) & -63.27075 & -31.63539 & -31.63549 & -31.63540 & -31.63532 & -63.27093 & -48.73654 & -31.63247 \\ E_{\mu}(aumo)(eV) & -65.53833 & -32.20226 & -32.76916 & -32.35994 & -33.13145 & -66.98746 & -48.73660 & -31.63537 \\ \omega(10^{13} road/s) & 49.7272 & 26.4826 & 11.9890 & 17.8228 & 13.3984 & 19.0113 & 68.9812 & 44.1776 \\ E_{\mu}(eV) & -0.35806 & -0.26130 & -0.18211 & -0.21927 & -0.19465 & -0.23440 & -0.42172 & -0.33749 \\ E_{\mu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{\mu\mu\nu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{\mu\mu\nu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{\mu\mu\nu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{\mu\mu\nu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{\mu\mu\nu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{\mu\mu\nu}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.1$	<i>c</i> ₃	0	1	0	0	0	0		
$ \begin{array}{c} C_{2e} & 0.85252 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ V_{e}(eV) & -101.12679 & -37.10024 & -32.76465 & -31.36351 & -34.04658 & -106.90919 & -78.97795 & -40.92709 \\ V_{e}(eV) & 20.69825 & 13.17125 & 10.10870 & 9.67426 & 10.49024 & 23.57588 & 28.90735 & 14.81988 \\ T_{e}(eV) & 34.31559 & 11.58941 & 9.04312 & 7.92833 & 10.11966 & 40.12475 & 31.73641 & 16.18567 \\ V_{e}(eV) & -17.15779 & -5.79470 & -4.52156 & -3.96416 & 5.05983 & -20.06238 & -15.86820 & -8.09284 \\ E_{emin}(eV) & 0 & -14.63489 & -14.63489 & -14.63489 & 0 & -14.53414 & -13.6181 \\ \Delta E_{emin}(eV) & 0 & -11.3379 & -1.13379 & -0.72457 & -1.49608 & 0 & 0 & 0 \\ E_{emin}(eV) & 0 & -13.50110 & -13.50110 & -13.91032 & -13.13881 & 0 & -14.53414 & -13.6181 \\ E_{emin}(eV) & 0 & 0 & 0 & 0 & 0 & 0 & -14.53414 & -0.8881 \\ E_{emin}(eV) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -14.53414 & 0 \\ E_{emin}(eV) & 0 & -13.50110 & -13.50110 & -13.91032 & -13.13881 & 0 & -14.53414 & 0 \\ E_{emin}(eV) & -63.27075 & -31.63539 & -31.63549 & -31.63540 & -31.63532 & -63.27093 & 48.73654 & -31.63247 \\ E_{emin}(eV) & -65.53833 & -32.20226 & -32.76916 & -32.35994 & -33.13145 & -66.98746 & -48.73660 & -31.63537 \\ D_{emin}(eV) & -0.35866 & -0.26130 & -0.18211 & -0.21927 & -0.19465 & -0.23440 & -0.42172 & -0.33749 \\ E_{emin}(eV) & -0.25882 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{emin}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{emin}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{emin}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{emin}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{emin}(eV) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ E_{emin}(eV) & -0.4803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -0.14803 & -$	Cin	0.5	0.75	0.5	0.5	0.5	0.5		
$\begin{array}{c} V_{p}\left(eV\right) \\ V_{p}\left(eV\right) \\ 20.69825 \\ I3.17125 \\ I0.10870 \\ 9.67426 \\ I0.49024 \\ 23.57588 \\ 28.90735 \\ I1.8941 \\ I0.4924 \\ 23.57588 \\ 28.90735 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I4.81988 \\ I$	C ₂₀	0.85252	1	1	1	1		 	
$ \begin{array}{c} V_{p} (eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ Z(eV) \\ Z0.69825 \\ $	V. (eV)	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78,97795	-40.92709
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	V, (eV)	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	 	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	T (eV)	34.31559	11.58941	9.04312	7.92833	10.11966			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	<u></u>	-17.15779	-5.79470	-4.52156	-3.96416	5.05983			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	· · · · · · · · · · · · · · · · · · ·	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\Delta E_{H_{3},1,0}(AO/BO)$ (eV)	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$E_{I}(nino)$ (eV)	0	-13.50110	-13.50110	-13.91032	-13.13881	. 0	-14.53414	-13.6181
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0	0	0	0	. 0	0		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$E_{r}(atom-atom,msp^{3}.AO)$ (eV)	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$E_{\gamma}(in)$ (eV)	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66,98746	-48.73660	-31.63537
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\omega \left(10^{15} rad / s\right)$	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44.1776
$ \begin{array}{c} \overline{E}_{D}\left(eV\right) & -0.35806 & -0.26130 & -0.18211 & -0.21927 & -0.19465 & -0.23440 & -0.42172 & -0.33749 \\ \overline{E}_{Exts}\left(eV\right) & 0.19649 & 0.35532 & 0.15498 & 0.10539 & 0.12808 & 0.19342 & 0.40929 & 0.46311 \\ \underline{E}_{exc}\left(eV\right) & -0.25982 & -0.08364 & -0.10462 & -0.16658 & -0.13061 & -0.13769 & -0.21708 & -0.10594 \\ \overline{E}_{exc}\left(eV\right) & 0.14803 & 0.14803 & 0.14803 & 0.14803 & 0.14803 & 0.11441 & 0.14803 & 0.11441 \\ \overline{E}_{f}\left(\text{Group}\right)\left(eV\right) & -49.54347 & -32.28590 & -32.87379 & -32.52652 & -33.26206 & -67.26284 & -49.17075 & -31.74130 \\ \overline{E}_{exts}\left(e_{exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(\text{Exts}\left(E$	E_{κ} (eV)	32,73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ar{E}_{\!\scriptscriptstyle D}$ (eV)	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440		
$ \frac{E_{\text{crit}}(eV)}{E_{\text{crit}}(eV)} = \begin{array}{ccccccccccccccccccccccccccccccccccc$	Ē _{Keb} (eV)								
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$E_{total}(\epsilon, solido)(eV)$ -14.63489 -14.63489 -14.63489 -14.63489 -14.63489 -14.63489 -14.63489 -14.63489 -14.53414 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -13.6181 -1	$E_{r}(Group)$ (eV)	-49.54347	-32.28590	-32.87379	-32.52652	-33.26206			
E _{Indiat} (c. 40110) (eV) 0 -13.59844 0 0 0 0 -13.59844 -13.59844 -13.59844	$E_{lnRial}(\epsilon_{a}$, ω , $Ho)$ (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489		
F (a \ (a/V)	$E_{intual}(c, 30110) (eV)$	0	-13.59844	0	0	0	0		
	$E_D^{(Group)}(eV)$	5.63881	3.90454	3.60401	3.25674	3.99228	8.72329		

$E_{\rm max}$ is 250 commond to the receivment values $\Omega_{\rm L}$. The magnetic energy $E_{\rm m}$ that is subtracted from the weighted sum of the $E_{\rm L}(\rm loss)$ (e)	Table 15.253. The total bond energies of any nitro compounds calculated using the functional group composition and the energies of 18018 15.252 compared to the compound of the compound of the composition and the energies of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound of the compound o	values based on composition is given by (15.58). Values based on composition is given by (15.58). Total form of F Column Relative

					7.1	6.5	ĵ.	120 (50-52)	(benzene)	(benzene)	125.2 [54]	125.3 (nitronethane)	118.5 [54]	(nitrobenzene)	(phenol)	6611	(aniline)		
-	Епо	0046	-0.00070	2000	0	ار اور اور	<u> </u>	01 051		16'611		126.52	64.11	78.	109.84	113.80		170.05	
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Slealand	Total Bond	65.18754	77.61308	72.47476		12	`		-1,83556			-1.44915		-1.63376	0		7	c	,
	LU)	-	400	•		1	s* .		0.79732			0.81549		0.81670	17716.0		1.06823		2000
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	NH,	morn	0-			,	5		-			-		-	0.75		_		0.75
	~ 0						C ₃		0,79232			0.81549	0.85393	9 13 15 15 15 15 15 15 15 15 15 15 15 15 15	0.01771		_	0.84665	(Eq.
	, g	- 5	~ ~		40,40).		o Maria		0,79232			0.81549		0.77945	-	0,93613	P	0,84665	(Eq.
	C-0 (a)	door	• – •	00	5, (atom – atom, m		Atom / Hybridization Designation	(Table 15.3.A)	ž			z		٥		-	I		z
	C-N (b)	die	- 14		s (1). E. is		Contrade Atom 3		.17.17218			-16.68411		-13,61106		000	I		-14.53414
	() // (a)	ı	o o =		experimental values [1]. E_{τ} is $E_{\tau}(arom-arom,msp^2,AO)$		Atom 1 Hybridization Designation	(Table 153.A)	77			2		\$		-	z		6
	0.11.0		~ ~ ~		omds and	Daties min	Eranbarha Atom I		-17,17218			118,68411	•	-17.45362		-14.82575	-14.53414		.15.95955
	`	'			in com	1100	2c* Terreinal Atoms	3	4.5585			4,1231		4,4159		3.6315	3.1539		3,9833
15 CB)	1	2 -	~ ~ ~	. vc ve	e person a	s or anyt to	(e) 15's'		2 62936	-+-		2.30843		2,30×43		1.83616	I.SBZ6X		1,88268
) when he	P PINCH OF T					e parameter.	%] G	}	2,000	Т		1.30K43		2,81279		2.59399	1,38268		2,69190
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	tucs bas	duimor d	H,NO,	000 222 233		able 15.7	۲			٦	٣]							

BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an C-C(O)-OH moiety that comprises C=O and OH functional groups that are the same as those of carboxylic acids given in the corresponding section. The single bond of aryl carbon to the carbonyl carbon atom, C-C(O), is also a functional group. This group is also equivalent to the same group of carboxylic acids except that $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -1.29147~eV which is a linear combination of $\frac{-1.13379~eV}{2}$, $E_T(atom-atom,msp^3.AO)$ of the C-H group that the C-C(O) group replaces, and that of an independent $C2sp^3$ HO, -0.72457~eV (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas $C_7H_6O_2$, $C_7H_5O_2Cl$, and $C_7H_7NO_2$, respectively. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The NH_2 and C-N functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The C-Cl functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The C-Cl functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of 20 chlorobenzene, except that $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918 \, eV$ (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the $C2sp^3$ HO.

The symbols of the functional groups of benzoic acid compounds are given in Table 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each $E_D(Group)$ of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

5 Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
C-C(O)	C-C(O)
C=O (aryl carboxylic acid)	C = O
(O)C-O	C – O
OH group	OH
Cl - C (Cl to aromatic bond of 2-chlorobenzoic acid)	C-Cl (i)
Cl-C (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	C-Cl (ii)
Aryl C-N (aniline)	C-N
NH ₂ group	NH ₂

	Γ		T	٦	Г	Τ	_	Γ		Τ	
	WH.	Group	1 24730	07447'1	0.94134	1000	0.99627	0.998	(agibne)		0.81370
	C-N	Group	1 81158	20112	1,34595	1 43440	C4474.1	1.431	(militae)	131361	\$5717.1
	(E) C-3	Group	2.19358		1,64243	1.73877		1.737	(amagana)	1 45403	Contra
	0-0-0	Group	2.20799		1.64782	1,74397		1.737 (chlorobenzene)		1.46967	
	ж,	Cross	1.26430	200100	9/19/16/0	0.971651		0.972 (formic acid)		0.86925	0.77616
	0-0	dioip	1.73490	131716	01 (15:1)	1.39402		1.393 (methyl formate)		1.12915	0.75971
entel values [3].	0 • 0		1.29307	1.13977		1,20628		1.214 (acetic acid)		0.62331	0.87737
compounds and experimental values [1]	(<i>O</i>))) – 2	1 06111	11100	1.39682		1.47833		1.48 [55] (benzoic scid)	36676 1	1.3044.3	0.71591
and 19.630. The Ecometrical band parameters of benzoic acid comp	CH (i) Group	1 60061	100001	1.03299		1.09327		l.101 (benzene)	1 22265		0.64537
i ile geometricali oand pa	ري. ريون	1.47348		1,31468		1.39140		1.399 (benzene)	0.66340	0 0000	0.89223
10.2.20	Parameter	0 (0")		(%)	Bond Length	2c. (4)	Exp. Bond	Length (A)	h,c (a,)		

Table 13.237. The MO to HO intercept geometrical band parameters of benzoic acid compounds. Ly 18 127 (mini = mini, mily : mily	notrical Don	d parameters of L	שמונים במוני	portion to the	12. (millio – cum.	t and done			i						-
Bond	Aton	F. 1	F.,	1.5	Li'	Final Total	.1:	1	E.m. (C25)	E(C2sp²)	÷ 3	e (6 " (A. ((
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	(s 2)	(<u>e</u>)	(°)	Fine)	(oV)	 	Ξ	Ξ	(a)	(%)
C-H (C,H)	ú	-0,85035	-0,85055	-0.36690	٥	-153.88327	0.91771	0,79597	-17.09334	-16.90248	74.42	85.201	38.84	1.24678	0.21379
$C = H\zeta_{n}^{-N}$ $C = H(X, R)$ $C = H(X)X_{n}^{-N}C(H),$ $C = (C)X_{n}^{-N}C_{n}(H)$ $C = (H, N)C_{n}^{-N}C_{n}(H)$	ಶಲ್ಲಿಕ	-0,15035	0.85(35	06995'U-	0	-153.88327	0.91771	G.79597	-17.09334	-16.9024	134.24	45.76	58.92	0.75935	Q.55533
(C, =) C, (O) O - H	0	-0.9291x	c	c	۰		1.00000	0.86359	-15.75493		113.00	16.91	64.12	0,55182	0.36625
(C,*),C,(0)-OH	0	-0.9291K		0	0		1.0000	0.86359	-15.75493		25,101	78.68	#7.8	1.14763	0,16950
(C,=), C, (O) - OH	ن	.0.9201R	Abgle,1.	-0,64574	0	-154,54007	11716.0	0.76652	-17,75013	-17.55927	11.52	847.89	42.68	1,27551	0.04163
$\left(C_{s}^{1/2}\right)C_{s}(OH)=0$	c	.1.349Jlf	o		C		1,0000	0.84115	-16.17521		137.27	473	16.33	0.52193	0,61784
$\left(C_{h}^{N}\right)_{C_{h}}C_{h}(OH)=0$	٠٠	1.34946	-D, Gal 574	40.92918	0	-154.54007	17716.0	0,74452	-17,75013	-17.55927	134.03	43.77	62.14	0,60099	8/2520
(',=(H/XX',)C,=C, ((C, bound to H, C', or NH,)	ئ	-0,64574	-0.85035	-0.85035	0	-153.96212	17716.0	0.79232	.17,17218	-16,98132	134.09	45.91	58.79	0.76344	0.55124
(, a) (, - ()	Ö	(427)E.0-	0	0	c		1.03158	0.89582	15.18804		12,52	97.08	37.22	1,75824	0.11042
D~ J (=)	บ้	-0.36229	-0,85035	-0.85035	υ	-153.678.67	14216.0	0.80361	-16 HRR73	-16.697R6	73.22	104.61	79'16	11678,1	0.23129
C, =(C)X', =C, (C, bound to H or C!)	ن	4536.0-	-0.85035	0.85035	0	153.67867	0.91771	0.80561	-16,88873	•16.6978K	134.65	45.35	59.47	0.74854	0.56614
$\left(C_{s}^{H}\right)C_{s}NH-H$	*	-0.56690	c	0	0		0.93084	0.11392	-13,39265		121.74	51.26	67.49	0.47634	0,46300
(C, #) C, - NH;	Ų.	-0.56690	-0, R5035	52058.0-	0	-153,RE338	0.91771	0.79397	-17.09334	-16.90248	6F.181	91,51	41,01	1,36696	0 02101
$\left(C_{s}^{h}\right)_{s}^{h}C_{s}-NH_{s}$	2	0699Ş:O-	c c	0	0		0.93084	0,81392	-13,39265		96,32	13.68	46.43	1,24859	0.09736
C=(H,N)C,=C	Ů,	-0.25035	-0.85035	06995'0-	0	-153,88327	17716.0	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0,55533

Indie 15.256. The energy parameters (cv) of trunctional groups of energy controlled and component. Parameters	CaC CaC Orden	('H (i) Group	C-C(O)	C=0 Graup	C-C Group	Croup	C-CI (i) Group	C-C/ (ii) Group	C-N Group	NH ₃ Group
7,	0.75	_								
ř.	2	-	-	2	_	-	-	1	1	2
u u	0	0	0	0	0	0	0	0	0	0
n,	0	0		٥	0	a	0	0	0	1
<u>'</u>	6.5	0.75	5.0	0.5	5'0	0.75	0.5	0.5	0.5	0.75
	0.85252	_	_	-	-	-	0.81317	0.81317	-	0.93613
ان ن	-		-	-	-	0.75	1	-	1	0.75
ů.	0.85252	17716.0	0.91771	0.85395	0.85395	-	-	-	0.84665	0,92171
ű	c	_	•	2	٥	_	0	0	0	0
บั	.,	_	7	4	2	-	2	2	2	-
-5-	0	1	٥	0	0	-	0	٥	0	_ 2
ن	0.5	0.75	0.5	0,5	0.5	0,75	0.5	0.5	0.5	1.5
ر۸	0.85252		-	-	_	-	0.81317	0.81317	-	-
v, (eV)	-101,12679	-37.10024	-32.15216	-111,25473	-35.08488	40.92709	-31,85648	-32,14474	-32.76465	-78.97795
V, (eV)	20.69825	13.17125	9.74055	23.87467	10,32968	14.81988	8,25686	8.28394	10.10870	28.90735
T (uV)	34.31559	11.58941	8.23945	42.82081	10.11150	16.18567	7,21391	7.32700	9,04312	31,73641
7, (07)	-17.15779	-5.79470	4.11973	-21,41040	-5.05575	-8.09284	-3.60695	-3.66350	4.52156	-15.86820
E(m 10) (eV)	0	-14.63489	-14.63489	0	-14.63489	-13.6183	-14.63489	-14.63489	-14.63489	-14.53414
AE a, in (40 na) (eV)	o	-1,13379	-1,29147	-2,6893	-2.69893	٥	-2,99216	-2.99216	-1.13379	•
Er (10 00) (0V)	0	-13,50110	-13,34342	2.69893	-11,93596	-13.6181	-11.64273	-11.64273	-13.50110	-14,53414
F(4, so 10) (4V)	0	0	0	0	0	0	0	0	0	-14,53414
15, [u, sus) (eV)	-63.27075	-31,63539	-31.63530	-63.27074	-31,63541	-31,63247	-31,63539	-31.65542	-31.63549	-48.73654
Er (atom - atom, mist AD) (eV)	-2.26759	06995'0-	-1,29147	-2.69893	-1.85836	0	-0.72457	-0.92918	-1.13379	0
Er (1m) (cV)	-65,53833	-32,20226	-32,92684	-65.96965	-33.49375	-31.63537	-32.35994	-32.36455	-32,76916	-48.73660
(101: rad/s)	49.7272	26.4826	10,7262	59,4034	24.3637	44.1776	8.03459	8.11389	11.9890	68.9812
$E_{\mathbf{r}}$ (vV)	32.73133	17,43132	7.06019	39.10054	16.03660	29.07844	5.28851	5.34070	7,89138	45.40465
E, (eV)	-0.35806	-0.26130	-0.17309	-0.40804	-0.26535	-0.33749	-0.14722	-0.14888	-0.18211	-0.42172
Ext (eV)	0.19649	0.35532 Eq. (13.458)	0.10502	0,21077	0,14010	0.46311	0.08059	608000	8675[0 [54]	0.40929 [22]
E_ (eV)	-0.25982	-0.08364	-0.12058	-0.30266	-0.19530	-0.10594	-0.10693	-0.10859	-0.10462	-0.21708
For (cV)	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441	0.14803	0.14803	0,14803	0.14803
Er (rang) (cV)	49.34347	-32,28590	-33.04742	-66.57498	-33,68903	-31.74130	-32.46687	-52.67314	-32.87379	-49.17075
Emery los, so ist) (eV)	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-13.6181	-14.63489	-14.63489	-14,63489	-14.53414
E (4. 10. 110) (41)	0	-13,59844	0	0	0	-13.59844	0	0	0	-13,59844
$E_{\mu}(com)$ (eV)	5.63881	3.90454	3.77764	7.80660	4.41925	4.41035	3.19709	3.40336	3.60401	7.43973

, 034.31	See showman bine ninzana to seimment bear better the nation of the) comment	Chenzair e	min conne	mode calcut	cultated using the functional group composition and the energies of Table 15.238 compared in the experimental values 12	ctional group	composition and the	he energies o	fTable 15.2	38 comparen	th the exper	INCHIA VE	13. Sani			١		ł	ļ
ie 13.439.	ווכ נסופו סמומ	energies o			H G	(O)O-C	C=O	0-0	HO	٠ <u>-</u> ٠	C-C(()	C-C(II)	×-∵	×	WH,	Total Bond		stad Bond Es		Refative
Formula	Nanc		ည (ပီ (Group	Group	Group	Group	Group	Ğ,	Group	Grand	ğ	dn	Group	Energy.	1	20.	- }	3000
			CLOND	1		-	-	-	-			0	•		٥	27.5		2 5		0000
	Banzoie acid 2-ehforobenzoie seid	78			, 		۰ -			- 0		e -				73.26		13261		0000
	3-chlorobenzoie seid	. g	s -s				- -	. _	_	•	_	_ •	٠.	_	o -	73.268		13.24) RD 946		00043
CHING	Antico 2-carbon lia acid	Lie Beid	: •5 •		· • •						. .	۰۰				10,90257		80.813		1000
Į	Aniling 4-carboxy lie seid Aniling 4-carboxy lie seid	he sold	اء٠		, ,		-	+	_			c			_	90,00	1	242	1	
le 15.260.	Table (5.260. The band souls parameters of benzoic said compounds	s parameter	rs of benzo	nic acid co.	ne spanodus	d experimental va	Nues [1]. E,	and experimental values [1]. E_{r} is $E_{r}ig(\sigma tom-\sigma tom,nxp^{2},AOig)$	11, 11Xp2. AO).								f	- }		
Menuil Anglo	qty	'nΞ	24. Red 2	Teninal	Asm -	Alom 1 Hybridization	Cristal Area 2	Atom 2 Hybridization Designation	races 1	C ₂	ر. ت	ڻ		יע	ę.y.	o, ©	* ©	* ©		(e)
		(%)	<u>e</u>			(Table 15.3.A)		(Table 15.3.A)				-	-	1			+	+	-	100,140,531
לננג		262936	2.62936	4,5585	-17,17208	ı	-17.17218	*	0.70133	0 19732	-	_	- d	n.79233	.1.85836		-	ž	120.19	(penzene)
(aromatic)	H ()	T											-				120.19	119.91		tzo iso-szi (benzene)
(aromatic)	ii)	1000	77,76	, di 3, i	36364 71	-	.14.82575	-	-	0.91771	57.0	-	0.75	0.91771	0		H	107.71	5	
0.5.5	5, 0	282786		1471	81571,71-	, z	13.6120%	٥	0.7723	0.85395	-	-	-	CIECA!O	-1.63376			ŭ	121.86	122 (55) Den <i>e</i> zie acid)
0.0.0		, 10,00%	_		-16.40867	2	.13,61806	0	0.KZ959	0.85735 (Eq.	-	-	-	0.m.i77	-1.63376		-	=	117.43	118 (55) (berezole ardé)
	: 5	1 77954	3 (343)		16.17521	21	-15.75493	,	0.84115	0.86359	-	-	-	0.NSZ37	-1,44913		-	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	126.03	122 (55) (bonzaic seld)
V.0.4					31		54						-				-	-	-	120 (4CC(H)C
ענונ	į, (2.62936	2.62936	4.5585	KICT(,TI-	*	-17.1721H	z.	Q.79352	0.79232	-			0,79232	1,83836				ch.	chlorobenzene) 121.7 (ZCC (C1)C
(Samualo)																			€	chlorobenzene) (20 (50-52) (benzene)
1.3.37 H.3.37	# Z.																61,051	=	19.91	(benzene)
HNH2	# H	1,282/4	1, ##26#	3.1559	-14.53414	z	2	x	0,93613 Eq.	-	_	,	27.5	1.00923	۰			밀	(LE)	(401107C)
HN'. X7	HN.	2,69190		1,88268 3,9833	-15.05955	•	PIES PI	z	O.Burk65	0.84G65 (Eq.	0.73	_	0.73	000001	0			Ž	170.05	
																		֡		

ANISOLE

Anisole has the formula C_7H_8O and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety $-O-CH_3$ to form an ether comprising aromatic and methyl functional groups as well as two types of C-O functional groups, one 5 for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The CH_3 and methyl C-O functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The C-O functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether C-O functional group except that $\Delta E_{H_2MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -1.13379~eV (Eq. (14.247)). $E_T(atom-atom,msp^3.AO)$ is based on the energy match between the OCH_3 group and the $C2sp^3$ HO of the aryl group and is twice that of the aryl C-H group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Aryl C-O	C-O (a)
Methyl C-O	C-O (b)
CH, group	$C-H$ (CH_3)

0.0246

58.98

43.76

0.21379

38.84 42.40 46.10 44.25 40.30

93.00

105.58 101.15 R4.02

, <u>a</u>

(a) (d)

°.€

(°)

<u>ن</u> دار	() H.J	('-() (a)	C-0(b)	C-H(CH,)
Group	Group	Group	Group	Group
1.47348	1.60061	1.82682	1.80717	1.64920
1.31468	1.03299	1.35160	1.34431	1.04856
1.39140	1.09327	1.43047	1.42276	1,10974
1.397 avg. (phenol)	1.084 (phenol)			1.11 (avg.) (toluene)
0,66540	1.22265	1.22900	1,20776	127295
0.89223	0.64537	0.73986	0.74388	0.63580
	1.31468 1.39140 397 avg. phenol) 0.66540		1,60051 1,0329 1,09327 1,084 (phenol) 1,22265 0,64337	1,60061 1,82682 1,03299 1,33160 1,00327 1,43047 1,084 (phenol) 1,22265 1,22900 0,64337 0,73986

	6 0	14.42	78.85	95.98	93.18	87.00	92.19	134,24	
	$E(C2s\rho^2)$ (eV) Final	-16,90248	-13,35946	-15.35946		-16.90248		-16,90248	
	E(C2w') (oV) Final	NEE90.71.	-15.55033	13,53033	-16.11722	-17,09334	-16,11722	-17.09334	
	'j (<u>a</u>	0,79597	0.87495	0.87495	81346.0	0.79597	0.84418	0.79597	
	, a (a)	17710.0	17716.0	17716.0	1.00000	17710.0	1.0000	17719,0	
	Final Total Energy C'2sp ² (eV)	-153.8837	152,34026	-152.34026		-153,88327		-(53.8527	
msp'.AO).	E _r (eV) Bond 4	O	¢	Û	٥	6	0	0	
7, (arom – arom,	E, (eV) Bond 3	-0.36690		0	٥	-0.15035	0	-0.15035	0 46600
anisole. E, is I	E, (eV) Bond 2	-0,H5035		0	06995-0-	-0.85035	-0.72457	-0.K5(35	A #5014
1 parameters of a	Er (eV) Bond 1	-0.K3f335	-0.72457	-0.72457	-0.72457	A. 56690	-0.56590	-0.56690	-0 15015
netrical bond	Атоп	ئ	ů,	υ,	Э	ر.	0	٠,	5
Table 15.265. The MO to HO intercept geometrical band parameters of anisole. E_T is $E_T(anom-anom,mxp^2,AO)$	Bond	C-H (C,H)	C'-H (OC,H ₃)	(c,=) c,o-c,H,	(c.=),c.o-c.n,	(c, =), c, -oc, H,	(c, =), c, −oc, H,	$\left(C_{i}^{*}\right)^{C}$	(=(H)C;) C.OX; H.

Table 15.264. The energy parameters (eV.) of functional groups of anisoic.	s (eV) or tunction	al groups of an	sole.		
Parameters	ე≝ე Group	CH (C) Group	C = O (a) Group	C-0 (b) Group	CH ₃ Group
7,	0.75				
'n	2	-	-	1	3
n,	0	0	0	0	2
'n	0	0	0	0	0
ប័	0.5	0.75	0.5	0.5	0.75
<i>C</i> ₁	0.85252	1	-	1	1
c,	_	_	-	1	1
63	0.85252	17716.0	0.85395	0.85395	0.91771
ئ	0	1	0	0	0
ั้ง	3	1	ż	2	1
·S	0	-	0	0	3
'U'	0.5	0.75	0.5	9.5	0.75
رد.	0.85252	1	1	1	1
V, (eV)	-101.12679	-37,10024	-32.67197	-33.15757	-107.32728
V, (aV)	20.69825	13,17125	10.06645	10.12103	38.92728
T (eV)	34.31559	11.58941	8.94231	9.17389	32.53914
V, (eV)	-17.15779	-5.79470	-4.47115	-4.58695	-16.26957
E(wind) (eV)	o	-14.63489	-14.63489	-14.63489	-15.56407
$\Delta E_{D_1 M_2}(somo)$ (eV)	0	-1.13379	-1.13379	-1.44915	0
Er (20110) (eV)	0	-13.50110	-13.50110	-13.18574	-15.56407
E, (11.20) (eV)	-63.27075	-31.63539	-31.63547	-31,63533	-67.69451
$\mathcal{E}_{r}(atom - atom, msp^{3}.AO)$ (eV)	-2.26759	-0.56690	-1.13379	-1.44915	0
$E_{r}(\omega)$ (eV)	-65.53833	-32.20226	-32.76916	-33.08452	-67.69450
w (1013 rad/s)	. 49.7272	26.4826	11.8393	12.0329	24.9286
E_{K} (eV)	32.73133	17.43132	7.79284	7.92028	16.40846
\vec{E}_n (gV)	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
Eknt (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.13663 [21]	0.13663 [21]	0.35532 (Eq. (13.458))
Eine (eV)	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
Emis (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{r}(inw_{p})$ (eV)	-49.54347	-32.28590	-32.88182	-33.20040	-67.92207
Enthal (c. willo) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
Enter (r. 101110) (aV)	٥	-13,59844	0	0	-13.59844
E_{D} (inur) (eV)	5.63881	3.90454	3.61204	3.93062	12.49186

mental values [2].	Relative	Entor
ompared to the experi	Experimental	(eV)
of Table 15.264 c	Calculated	Energy (eV)
and the energies	CH,	Group
oup composition	C=0 (b)	Group
the runctional gr	C-0(3)	die.
Calculated using	() H.)	
ביאנים פו שוויפפום	ن ۱۱ ج	9
	Name	, se
	Formula	C,H,O Amis

	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1 1 0.1901 1.85836.		120 190
	9 (-	٠.
	9 ()	-		1	-
	E _r (eV)		.1.85836		
	w		0.79232		
	ซ	1	-	1	
	ď		_		
	ڻ ٽ	1	_	İ	
	C. Villa 2	1	0.79232		_
	ري ال ا		0.79232 0.79232		_
m, amp .Ac.).	Atom 2 Hybridizzion Designation (Table 15.2.a.)	Į.	*		
*(umin = 010	Eratuala Alan 3		-17.17218		
יין כא יום ביים ביים ביים ביים ביים ביים ביים	Atom 1 Hybridization Designation (Toble 15.3.A.)	,	•		
	Cranada Atra I		W 7, 1, 1, 1		_
	2¢' Yeminel Atems (a ₀)	20777		-	
	2¢' 0=41 (a,)	3500			
	(°)	350036 350536			
l		2007	(aromatic)	ACCA (Account)	(atomatic)

Table 15.266. The bond angle parameters of anisole and experi

PYRROLE

Pyrrole having the formula C₄H₅N comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a NH functional group. The two symmetrical carbon-to-nitrogen bonds comprise the C-N-C functional group. The 1,3-5 but diene moiety comprises C-C, C=C, and CH functional groups. The C-C and C = C groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-but diene except that the hybridization terms c_2 of the C-C10 and C = C groups and C_2 and C_{20} of the C = C group in Eqs. (15.42) and (15.52) become of benzene given that Εq. b y (15.143). $(C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = 0.85252$), in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond 15 character in the carbon-heteroatom bonding.

The NH group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term c_2 is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the CH functional group is equivalent to that of 1,3-butdiene, except that $\Delta E_{H_2MO}(AO/HO) = -2.26758 \, eV$ (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the C-N-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ N) = 0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2o} in Eqs. (15.42) and (15.52).

become that of benzene given by Eq. (15.143), C_2 (benzeneC2sp³HO) = 0.85252. Furthermore, ΔE_{H_1MO} (AO/HO) in Eq. (15.42) and E_r (atom-atom, msp³.AO) in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom corresponding to -3.71673 eV in total. This is the maximum energy for a single bond and corresponds to methylene character as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

15 Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	Group Symbol	
$C_a = C_b$ double bond	C = C	
$C_b - C_b$	C-C	
$C_o - N - C_o$	C-N-C	
NH group CH	NH	\exists
СН	СН	

	CH	Group	1.53380	1.01120	1.07021	1.076 (pyrrole)	1.15326	00000
	NH	Group	1.24428	0.94134	0.996270	0.996 (pyrrole)	0.81370	63736 0
erimental values [1].	C-N-C	Group	1.43222	1.29614	1.37178	1.370 (pyrrole)	0.60931	0 00400
etrical bond parameters of pyrrole and experimental values [1],	2-2	Group	1.77965	1,33404	1.41188	1.417 (pyrrole)	1.17792	0.74961
geometrical bond paran	C = C	Group	1.45103	1.30463	1.38076	1.382 (pyrrole)	0.63517	0.89910
Table 15.268. The geom	Parameter		a (a ₀)	$c'(a_0)$	Bond Length $2c'$ (A)	Exp. Bond Length (A)	b,c (a_0)	ø

Table 13.20%. The MO to HO intercept geometrical bo	netrical bor	nd parameters of	and parameters of pyrrole. R_i is an alkyl group and R_iR_i , R^i are H or alkyl groups. E_i is E_i (and $i=0$ and $i=0$).	n alkyl group an	d R.R., R" are	H or alkyi grot	198. E, is E,	atom - atom,	nxp'.40)					
Bond	Atom	1,1	-57	£,	E_{γ}	Final Total]]3	$E_{con}(CLm^2)$	16(22.03)	.0	8	æ	,
		(°V)	(3)	<u>ئ</u>	(e)	Energy	13	(<u>S</u>	() : · · ·	. 3	-3	· 3	٢.
		Bond I	Bond 2	Bond 3	Bond 4	('2'm')	3	(0)	Final	Final (Ξ	<u> </u>	e E	(°)
C-H (C,H)	ن	-1,13340	\$1626'0-	e	0	-153.67867	1,417.1	0.80561	-16,88873	-16.69786	83.33	1770	73.07	2501
('- H (r' H)	;													20001.1
" - " () " () " - "		-1,13380	-1.1380	•	٥	-155,88328	17716.0	0,79597	-17,09334	-16.90248	1771	97.79	43.14	1 3 1934
$(C = (H)C - C \cdot (H) = C$		UALL!	13700								Ī			
	,		August.	>	9	-133.883.28	0.91771	0.79597	-[7,09334	-16.90248	1516	\$8.43	4249	131226
$(C_{*} = C_{*}(H)(H)C_{*} = C_{*}$	ڻ	-1.13310	OREE !!		0	-153.88328	17716.0	0.79597	-17.09334	X7206 91-	12.6 26	73.57	2000	Lines of
האת - י. (ה)	ļ										2000	40.00	13.60	/CW7/:
(u) * "	١,	-1,13380	X16260-	ē		-153,67867	177160	0.80561	-16,88873	-15.69786	136.75	43.25	50.35	PAZE IL D
(',(H)N-(',=C',(H)	۲,	-1.13380	81626.0-	٥		-153.67267	174100	0.00561	11. 00077	,,,,,,,		1		
(1) 11 11 11 11								2000	- to-woods	10,057.80	178.74	8	60.10	0.69253
$(u)^* = (u)^*$	2	-0.92918	81626'0-	٥	c		0.930¥4	0,81549	-16,68411		138.92	80.77	63.19	271170
N-H (NH)	ν.	-0.92918	. 10000	٩			1.1.2							Citra (4)
			-	,		_	0.9304	0.H 349	- C.684	_	11.2	39.09	00.03	

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Table 15.270. The energy parameters	C = C	C - C	C-N-C	NH	СН
	Group	Group	Group	Group	Group
$n_{\rm l}$	2	1	2	1	1
n ₂	0	0	0	0	0
n,	0	0	0	0	0
C ₁	0.5	0.5	0.5	0.75	0.75
<i>C</i> ,	0.85252	1	0.85252	0.93613	1
<i>c</i> ₁	1	1	1	0.75	1
<i>c</i> ₂	0.85252	0.85252	0.84665	0.92171	0.91771
C ₃	0	0	0	1	1
<i>c</i> ₄	4	2	4	1	Ī
<i>c</i> ₅	0	0	0	1	1
$C_{i_{\mathfrak{p}}}$	0.5	0.5	0.5	0.75	0.75
$C_{2\omega}$	0.85252	1	0.85252	1	1
V _c (eV)	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
V, (eV)	20.85777	10.19898	20.99432	14.45367	13.45505
T (eV)	35.96751	9.49831	37.21047	15.86820	12.74462
$V_{n}(eV)$	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
E(лотно) (eV)	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2MO}(\lambda O) (eV)$	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_{T}(AOIHO)$ (eV)	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_{r}(atom-atom, msp^{3}.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0	0
$E_r(\omega)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	15.4421	12.3131	15.7474	48.7771	28.9084
E_{κ} (eV)	10.16428	8.10471	10.36521	32.10594	19.02803
$\bar{E}_{_D}$ (eV)	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\overline{E}_{K\!nb}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
\bar{E}_{ore} (eV)	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
E_{mog} (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\gamma}(Gnap)$ (eV)	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
$E_{inuted}(\epsilon_i MOIHO) (eV)$	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{inited}(c, AOIHO)$ (eV)	0	0	0	-13.59844	-13.59844
$E_{D}(Group)$ (eV)	7.23317	4.74998	8.76298	3.51208	3.32988

if values (2)	,			ı
experiments	Relative	Error		-0,00057
5.270 compared to the	Experimental	Total Bond Energy	ج	44.785
nergies of Table 1	Calculated	Total Bond	Energy (eV)	44.81090
ition and the e	CH			7
roup compos	HN			-
the functional g	.)~ N ~ .)			-
calculated using	<u>ر</u> -ز			
1. The total bond energies of pyrrole o	U#U sursv			, tore
Table 15.27	Clamor		2 2	

Alter of Augle 7 7 7					()								and advanced by the						
	(a,)	(a,)	Transmel Atems (a _n)	Aires I	Hybridization Designation (Table 15.3.8)	Alom 3	Atom 2 Hybridization Designation	C ₂	Alon 3	ن .	ີ່	5	יצ'	E _r (cV)	(•)	9.	(c) (c)	8 Exp. 8	6
CH."N	1,02241	1.59228	40166	-14 K2575	-	-14.53414	z	17716.0	0.92171	57.0	-	27.0	.00435	0		-	120.51	51 [21.5]	
H.3*.37																13.00	27.01		6
ZHW."	I.RAZKA	2.5922X	3.8987	-14,53414	z	-16,49325	's	0.84665 (Eq.	0,82493 (Eq.	87.0	-	27.0	0.97435	0	2	+	120.37	1	
55.5'HZ	2.02241	2 66307	4,2111	-16,XKH73	21	-15,95954 C.	ų	0.80561	0.83232	87.0	-	0.75	1.05872	•	_	+	127.20	127.1	
7H,C,C,	1,02241	2,60925	4211	-16.XXX73	2	15,95054	2	0.80561	0.85252	67.0	-	6.73	1.05822	0		+	130 %	_	
".J".]"H7	2.02241	2,60925	11312	-17,09334 C.	×	-16.47951	=	0.79597	0.17562	6.73	-	6.73	1,03728			+	7 7.		
'H'.)".)7													1		= =	10.501 37.561			
ZNC,C,	2.59228	2,60925	4.1932	-14.53414	2	.17,09334 C,	=	0.84665 (Eq.	0.79597	-	-	-	0.82131	-1,44915	2			٩	
Z(', NC',	1.59228	2.59228	4,2426	17.81791	38	107.18.71-	92	0.76360	0.74360	-	-	-	0,76360	-1,85836	-	1	1 2		
, '.'.'.'.	2.60925	2.66807	4.2426	-17.KI79!	36	-18.02252	29	0.76360	0,75493	-	-	-	0.75927	-1.85136	_	+	10701	(pyrrale)	
															_				•

FURAN

Furan having the formula C_4H_4O comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the C-O-C functional group. The 1,3-butdiene moiety comprises C-C, C=C, and CH functional groups. The CH, C-C, and C=C groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The C-O-C functional group of furan is solved in a similar manner as that of the C-N-C group of pyrrole. The solution of the C-O-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy 10 minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-O-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ O) = 0.79329$ (Eq. (15.150)) matches the double-15 bond character of the $C2sp^3$ HOs to the O atom, and C_2 and C_{2o} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO) = 0.85252$. Furthermore, $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) is $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of furan are given in Table 15.273. The structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.276 corresponding to functional-group composition of the molecule.

25 The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

ups of furan.	Group Symbol	J=3	.))	J-0-D	H.J.
Table 15.273. The symbols of functional groups of furan.	Functional Group	C, = C, double band	(', -(',	" - 0 - C"	5

	_			,				_
	HU	Group	1.53380	1.01120	1.07021	1.075 (furan)	1.15326	0.65928
nental values [1].	C-0-C	Group	1,41546	1.28854	1,36373	1.362 (furan)	0.58583	0.91033
The geometrical bond parameters of furan and experimental values [1].	د. <u>-</u> ن	Gram	1.77965	1.33404	1.41188	1.431 (Airan)	1.17792	0.74961
geometrical bond param	رَجر	Group	1,45103	1,30463	1.38076	1.361 (furan)	0.63517	0.89910
Table 15.274. The	Parameter		a (a,)	c. (va)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a,)	

i_{τ} is $E_{\tau}(\sigma \iota \sigma m - \sigma \iota \sigma m, m s p', AO)$.	
is an alkyl group and R.R.R" are H or alkyl groups.	
ometrical bond parameters of furan.	
Table 15.275. The MO to HO intercept geo	365

						L	(A) of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the contract of the con	1							
00.0	Atom	ا (eV) Bond ا	Er (eV) Bond 2	E ₇ (eV) Bond 3	E _r (eV) Bond 4	Final Total Energy C2sp ²	[a]	7.8	E _{rre} (C2tp²) (eV) Final	E(C2sp²) (eV) Finel	.s ©	· (e)	, (°)	(a,)	(a,)
- H (C H)	; 					Š				!				_	
()	-	-1.13380	-0.92918	0	•	-153.67867	0.91771	0.80561	-16.88873	-16.69786	8335	39 96	73.67	1,10463	
- H (C,H)		13380	12200	,	,								15:52	1.10432	0.09351
117	•		00001.1	,	5	-153.88328	0.91773	0.79597	-17.09334	-16,90248	82.21	97.79	43.14	1,11914	0.10794
$-(H)C_{r}-C_{r}(H)=C_{r}$	ن	-1,13380	-1.13380	0	0	.153.88328	17710	0.79597	-17.09334	-16.90248	23.10	88.42	9,5		
=C (H)(H)C =C	ļ	, ,,,,,,									,	00.43	44.47	977157	0.02177
V - V - V	-	-1.13380	-1.13380	٥	•	-153.88328	17716.0	0.79597	-17.09334	-16.90248	136.36	43.64	98 65	0.72867	207530
$C_{i} = C_{i}(H)$	ن-	-1.13380	-0.92918	0		-153.67867	122100	0.20561	14 00073	7050771					0.07000
0-C =C (H)	,							0,000	-10.000/3	-10.09/80	130.73	43.25	5025	0.71784	0.58678
1		-1.13380	-0.92918	٥	0	-153.67867	17719.0	0.80561	-16.88873	-16.69786	140.16	39.84	61.75	0 66000	676170
$O-C_s = C_s(H)$	2	-0.92918	-0.92918	0	0		1 00000	0.81540	11 404 11					20000	700100
								2000	11400001		140.37	39.48	62.25	0.65906	0.62947
											į				

Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	$C = \overline{C}$ Group	C−C Group	C-O-C Group	<i>CH</i> Group
n_1	2	1	2	}
n_2	0	0	0	. 0
n ₃	0	0	0	0
C,	0.5	0.5	0.5	0.75
C_2	0.85252	1	0.85252	1
c_1	1	1	1	1
c_2	0.85252	0.85252	0.79329	0.91771
<i>c</i> ₃	0	0	0	1
c ₄	4	2	4	1
c _s	0	0	0	1
C_{1o}	0.5	0.5	0.5	0.75
C ₂₀	0.85252	1	0.85252	1
V (eV)	-104.37986	-33.80733	-102.49036	-39.09538
$V_{p}(eV)$	20.85777	10.19898	21.11822	13.45505
T (eV)	35.96751	9.49831	36.20391	12.74462
$V_{n}(eV)$	-17.98376	-4.74915	-18.10196	-6.37231
E(лоіно) (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-2.26759	-1.85836	0	-2.26758
$E_T(AOIHO)$ (eV)	2.26759	-12.77653	0	-12.36731
$E_T(H_1MR)$ (eV)	-63.27075	-31.63572	-63.27019	-31.63533
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0
$E_r(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	15.4421	12.3131	58.0664	28.9084
$E_{\kappa}(eV)$	10.16428	8.10471	38.22034	19.02803
$\overline{\overline{E}}_{D}(eV)$	-0.20668	-0.19095	-0.40965	-0.27301
$\overline{\overline{E}}_{Krib}(eV)$	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
\widetilde{E}_{usc} (eV)	-0.11720	-0.11680	-0.34704	-0.07587
$E_{mag}(eV)$	0.14803	0.14803	0.14803	0.14803
$E_T(cirmp) (eV)$	-65.77272	-34.01976	-67.68154	-31.71124
$E_{initial}(c_{\bullet} AOIHO) (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
$E_{initial}(c, AOIHO) (eV)$	0	0	0	-13.59844
$E_{D}(cirmp) (eV)$	7.23317	4.74998	9.14198	3.32988

and the energies of Table 15.276 compared to the experimental values [2].
ation a
C-0-C
調り
C = C
/. The total bond energies of Name
Formula

Table 15.278. The bond angle parameters of furan and experimental	angle paran	neters of fi	uran and e	xperimenta	I values [1]. In the calculation of θ , the narrameters from the measurement of	calculation	of θ , the namen	to much			-	, ,		27					
Anims of Angle	1,72	20,	2.7.5	6	A from 1		Amina da ana ana	in time in	e precenting	angic were	used. L	15 £7 (alo	n – alom, m						
	(a,)	(a ₀)	Terminal Atenta (a,)	Conton No	Hybridization Designation	Conbrate Atom 2	Ilybridization Designation	6. 5. m	C ₂	ហ	ູ້	ۍ	ν.	(eV)	ø, ©	6.0	9.3	(c)	Exp. 0
		-			(Table 15.3 B)		(Table 15.3.B)								;	 :		_	:
O*:3H7	1.02201	2.57707	257707 3.9328	-16.88873	51	-13.61806	0	0.8056?	0.79329 Eq	6.75	-	0.75	0.98470	6		+	+		1150
ZC,C,H,		L				T	·		(18,150)					,		-	_	17.02	(fumil)
0.0 11/				-16,88873		7,0000										117.02	110.69	132.29	
4.19.79.07	2.0224	2.66807	4.2269	ť	51	3	٠	0.80561	0.83252	27.0	_	0.73	1.05822			-	4-		128.0
ZH,C.C.	202241	2 60025	976.7	-16.88873		15.95954				1				>			_	128.09	(furan)
			_	٠,	2	ť	•	0.80561	0.85252	0.75	_	0.75	1.05822			-	Ŀ		
"5'C'C"	2.02241	2.60925 4.1312	4.1312	-17.09334	2	-16.47951	:			1				,		1	=	131.32	
				٠	2	ن.	=	0.70597	0.82562	2,2	-	0.75	1.03725	•			-	72.36.1	
7C,C,H,			_									\dagger			1		-	0.70	
7,5,5				-17,09334											-	123.76 107	107.01	127.23	128.0
(1,1,1)	2.60925	2.57707	4.2661	تن	82	-13.61806	0	0.79597	C. 7329	_		_	0 70463	20037		-	╀	-	(unu
	2,57707	2.57707	41231	-18 22713	9				(13.150))	1				0/650-1-	_		=_	69:01	(furan)
1000					2		or	0.74646	0.74646	-	_	_	0.74646	-1.85836		-	٤	102.36	106.6
*.,"^"., *	2.60925	2.60925 2.66807 4.2426 -17.81791	4.2426	17.81.791	92	-18.02252	29	03636.0	2075600	·	1	\dagger	\dagger		+	+	٤	9	(furan)

THIOPHENE

Thiophene having the formula C_4H_4S comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the C-S-C functional group. The 1,3-butdiene moiety comprises C-C, C=C, and CH functional groups. The CH, C-C, and C=C groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The C-S-C functional group of thiophene is solved in a similar manner as that of the C-N-C group of pyrrole and the C-O-C group of furan. The solution of the C-S-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between two $C2sp^3$ HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-S-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron 15 and proton of H given by Eq. (1.243). Thus, c_2 in Eq. (15.52) is $c_2(benzeneC2sp^3HO) = 0.85252$ to match the double-bond character of the $C2sp^3$ HOs, and the energy matching condition is further determined by the C_2 parameter. Using the energy of S, $E(S) = -10.36001 \, eV$ in Eq. (15.68) and the $C2sp^3$ HO energy of $E(C,2sp^3) = -15.76868 \, eV$ (Eq. (15.18) corresponding to s=2 in Eqs. (15.18-15.20), the 20 hybridization factor C_2 of Eq. (15.52) for the C-S-C-bond MO is

$$C_2(S3p \text{ to aryl-type } C2sp^3HO) = \frac{E(S,3p)}{E(C,2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700$$
 (15.153)

 C_{10} is also given by Eq. (15.153). Furthermore, $\Delta E_{H_2MO}(AO/HO)$ of the C-S-C-bond MO in Eq. (15.42) and $E_r(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -0.72457~eV per atom corresponding to -2.89830~eV in total. The energy contribution equivalent to that of 25 a methyl group (Eq. (14.151)) and that of the C-S-bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the $C2sp^3$ HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.282 corresponding to functional-group composition of the molecule. The bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	C = C
$C_b - C_b$	C – C
$C_a - S - C_a$	C-S-C
СН	СН

	_	_		_		т		
	#J	Group	1.53380	1.01120	1.07021	1.078 (thiophene)	1.15326	00000
merimental value (1)	C_s-C	Croup	1.74058	1.62766	1.72264	1.714 (thiophene)	0.61671	19100
14376 13.280. The geometrical bond parameters of thiophene and experimental values [1]	υ-υ- υ-υ-	drond	1.77965	1,33404	1,41188	1.423 (thiophene)	1,17792	0.74961
e gcometrical bond paran)=)	200	1.45103	1.30463	1,38076	1.370 (thiophene)	0.63517	0.89910
1837E 13.280. Int	Parameter		u (u,)	$c'(a_a)$	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (u_0)	8

T is F (alone - alon)	LT is it (will and into AD).	$r_{c} = \frac{E_{c} - (C2\mu)}{ E_{c} } \frac{E(C2\mu)}{ E_{c} } \theta$
?" are H or alkyl groups	edno e mili Biorba	Final Total
R is an alkyl group and R.R'.		E, ' E,
ameters of thiophene.		r &
cometrical bond par	TO, V	7
The MO to HO intercept ge		
.187.61	פַּ	!

Dana			-				ndanie (COP. destruction many des es de marco es en						
	Atom	(cV) Bond 1	(eV) Bond 2	E, (eV) Bond 3	E _r (eV) Bond 4	Final Total Energy C.2xp ¹	(a _o)	(°c)	Ec. (C210') (eV) Final	$E(C2sp^3)$ (eV) Final	, (o)	(°)	(°)	(a,)	(°°)
(C-H(C,H)		Date! 1	27.50			(6,4)									
(1, 2) 11 13		2000	-0.12431		0	-153.47406	0.91771	0,81549	-16.68412	-16.49326	84.49	95.51	44.74	1,08951	0.00011
(H') H = 1	 -	-1.13380	-1.13380	۰	٥	-153.88328	1771 0.0	0.79597	17 00 TL	14.00340		į			660.00
$(C_{*} = (H)C_{*} - C_{*}(H) = C_{*}$	ز	יפננו	1							0.50540	1779	87.76	43.14	1.11914	0,10794
	•		No. C. L.	>	0	-153.88328	0.91771	0.79597	-17.09334	16.90248	15.16	88.43	42.49	72275	151500
")="\"\(\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	ਹ ਂ	-1.13380	-1.13380	٥	0	20188121	122,100	0 70507							4.05177
SC = C(H)							2000	0.19397	-17.09334	-16.90248	136,36	43.64	59.86	0.72857	0.57606
	,•	-1.13380	-0.72457	•	0	-153.47406	17710	0.81549	-16 68417	76000	11217	1			
(H)" = " S".)	ن	081111	C3457.0-	,	,					mean'n la	137.10	42.86	60.85	0.70683	0.59777
(1) (1)			0,72031	,	5	-153,47406	0.91771	0.81549	-16.68412	-16.49326	141.52	38.48	95.33	0.08026	OVELYO
(H)" = " = (")	S	-0.72457	-0 72457	٥	•		1.3201	0.83600	00777.91.						2000
											7 7 7	-	,,,	-	-

Table 13.262. The effelty parameters (ev.) of innoughal groups of importance	is (ev) or ignorial	al Eldaps of Hillips	Jello.	
Parameters	ე≕ე Granb	C'-C Group	C-S-C Group	CH Group
u^{i}	2	1	7	-
n_{j}	0	0	0	0
σ_{j}	0	0	0	0
บ	0.5	0.5	0.5	0.75
৳	0.85252	-	0.65700	-
5	-	-	1	-
6	0.85252	0.85252	0.85252	0.9177
ড	0	0	0	-
່ວ	Þ	2	4	-
<i>c</i> ₃	0	0	0	1
ر!•	0.5	0.5	5.0	0.75
C ₂₀	0.85252	1	00/59'0	-
V, (aV)	-104.37986	-33.80733	-96.78916	-39.0953
V, (eV)	20.85777	10,19898	16.71820	13.4550
T (aV)	35,96751	9,49831	27.80371	12.7446
V. (0V)	-17.98376	4.74915	-13.90186	-6,3723
Elsosso) (eV)	0	-14,63489	0	-14,6348
DEnino (wo in) (eV)	-2.26759	-1,85836	-2.89830	-1.2675
15, (20 m) (eV)	2.26759	-12.77653	2.89830	-12.3673
$E_{\mathbf{r}}(u,\omega)$ (eV)	-63.27075	-31.63572	-63.27080	-31.6353
$E_T(alom - alom, mxp^2, AO) (aV)$	-2.26759	-2,26759	-2.89830	0
Fr (10) (0V)	-65.53833	-33.90295	50691.99-	-31,635
ω (10 ¹³ πυd/s)	15.4421	12,3131	10,3184	28.908
E_{κ} (cV)	10.16428	8.10471	6.79173	19.0280
E_n (aV)	-0.20668	-0.19095	-0.17058	-0.2730
End (eV)	0.17897	0.14829	0.08146	0.39427
E (01)	-0.11720	-0.11680	-0.12985	-0.0758
E_{mp} (cV)	0.14803	0.14803	0.14803	0.1480
Fylimus (eV)	-65.77272	-34,01976	-66.42873	-31.7112
Exert (r. in no) (cV)	-14.63489	-14.63489	-14.63489	-14.6348
Emisso (c. 10 mo) (aV)	0	0	O	-13,5984
$E_{p}(i_{max})$ (CV)	7.23317	4.74998	7.88917	3,3298

the experimental values [2].
.282 compared to
rgics of Table 15
Composition and the ene
the functional group
C-C
Ges of thiophen
Name
Formula

		$\begin{array}{c c} \theta & \text{Exp. } \theta \\ \hline \end{array} $:	_	(thicphene)	28	124.3				-			_	(thiophene)	653	=	1
		g ©	· 	119.58		.84 124.58	1 25	<u>:</u>	134 63	<u>: </u>	123.13	i	123.27		\$	-	¥. ≅	
		6 6	<i>:</i> 		4	119.58 115.84	\vdash	_	_	1		4	13.60	-	_	-		
		9 (0)	<u></u>	-	1	119		_		+		1	123.13	-				
(0)	m, msp. AO).	E _r (eV)		0					0		0			-0 77457		, 6000	-1.62836	
/	acom – ac	٧		0.87495			1.04540		1.04540	1	1.02453	1		0.71030		0831840	٠٠٠١٥٠٠	
	57 IS 57	G.		0.75			0.75		6.75		0.75			-		_	-	
boot erev	were used.			0.76144 (Eq.	15.126))		1		_		-			0.65700 Eq.	(15 153)	_		
tine and	and and	ប		0.73			27,0		0.75		0.73			_		_		
n the preces		C3		0.76144 (Eq.	13.125))		0.85252	1	0.85252		0.81549	\dagger		0.65700 Eq.	((5,153))	0.81549	1	
ameters from		Alem .		0.87495 Eq.	(G)C)		0.81549		0.81549		0.79597			0.76360	1	0.81549	1	
ion of θ , the pan	A trom 9	Hybridization Designation	(Table 15.3.B)	s			y		v	:	•			L/s		7		
n the calculat		Corbonite Aten 2		-10,36001		16 06061	, "C	-13.95954	<u>ن</u>	-16.68412	ڻ.			1003E.01-		-16.68412		
ental values [1]. 1	Atom	Hybridization Designation	(Table 15.3.B)	. 			7		4		:			7.2		▼	:	
und experim		Certesale Akm 1		-15.55033		-16 68417	ď	-16.68412	∵*	-17.09334	* 5		1401701	u*	1	-10.08412		
iophene a	20'	Tcmical Atoms (a,)		4.6030			4.1633		4.1633	4.0825				4.9809	4 70 69	*. 143e	93177	
eters of th	2.5.	(00)		3,25533			2.66807	2 60000	2.00/23 4.1033	2,60025				3,25533	1,1661,1		2,6807	
ngle param	2c,	β _{mad} ((α ₀)		2,02241			2.02241	, 60	7,024	2.02341			Γ	2.60925	1,74411		2 50003 5	
Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of θ, the parameters from the prezeding many ways and ε is ε form.	Alona of Angla			S,ZHZ	"H"."		ZH,C,C,	22 47	7,74	"J";"/7		ZC,C,H,		ZC,C,S	38:37	, U	7C.C.C.	

IMIDAZOLE

Imidazole having the formula $C_3H_4N_2$ comprises a conjugated system that is equivalent to pyrrole with one of the conjugated CH groups replaced by a nitrogen atom. The CH, NH, and C=C groups are equivalent to the corresponding groups of pyrrole, 5 furan, and thiophene where present. In addition, the nitrogen substitution creates a C-N=C moiety comprising C-N and N=C functional groups. The C-N bonding is the same as that of a tertiary amine except that the hybridization term c_2 in Eqs. (15.42) and (15.52) is that of the amino group of aniline, $c_2(arylC2sp^3HO\ to\ N) = 0.84665$ (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.42) and 10 other orbitals of the molecule. $E_{T}(atom-atom, msp^{3}.AO)$ in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)). This matches the energy of the group to that of the contiguous N=C group wherein $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.42) and $E_{\tau}(atom-atom,msp^3.AO)$ in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom of the double bond with aromatic character as in the 15 case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene, $n_1 = 2$ and C_2 and C_{20} are the same as C_2 (benzeneC2sp³HO) = 0.85252 (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the $C2sp^3$ HO, c_2 of the N=C-bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the C-N-C group.

As in the case of pyrrole, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ N) = 0.84665$ (Eq. (15.152)) matches the double-bond character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2n} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO) = 0.85252$. Furthermore, $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-0.92918\ eV$ (Eq. (14.513)) per atom corresponding to $-3.71673\ eV$ in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

10 Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	C = C
$N_b = C_c$ double bond	N = C
$C_b - N_b$	C-N
$C_o - N_o - C_c$	C-N-C
N_aH group	NH
СН	СН

Parameter	ンニン	תC	≯ 10	じーメーン	NH	Ť
	Granp	Group	Group	Group	Group	Group
a (a,)	1.45103	1.44926	1.82450	1.43222	1.24428	1.53380
c' (a,)	1,30463	1.30383	1.35074	1.29614	0.94134	1.01120
Bond Length 2c' (A)	1.38076	137991	1,42956	1,37178	0.996270	1,07021
Exp. Bond Length (A)	1.382 (pytrole)			1,370 (pyrrole)	0,996 (pyrrole)	1,076 (pymole)
h,c (a,)	0.63517	0.63276	1,22650	0.60931	0.81370	1.15326
"	0.89910	0.89965	11072 0	0 90499	0.75653	0.6592R

Table 15.287. The MO to HO intercept geometrical band parameters of imid	netrical bon	d parameters of i	imidazole. R _i i	descole. R_i is an alkyl group and $R_iR_i^*R^*$ are H or alkyl groups. E_i is $E_j\left(atom-\sigma tom, nxp^2,AO\right)$	and R.R.R" ar	e H or alkyl g	roups. Er is	E, (atom - do	", msp3, AO).						
Bond	Atom	(eV) Bond I	Er (eV) Bond 2	F ₁ (eV) Bond 3	E _r (eV) Bond 4	Final Total Energy (.2xp² (eV)	(a ₀)	'' (a°)	ε _r (C2τρ') (eV) Final	$E(C2p^3)$ (cV) Final	.6)	6 ©	e, (°)	(°)	(a,)
$(C-H^{\dagger}(C,H))$	٠,	-1.13380	-0.92918	o	0	-153.67867	17716.0	0.80561	-16.88873	-16.69786	83.35	96.65	43.94	1,10452	1 (160.0
$C-H\left\{ C,H\right\}$	ζ)	-1.13380	-0.46459	0	0	-153.21408	17716.0	0.82840	-16.42414	-16.23327	85.93	94.07	45.77	1.06995	0.05875
('-H (C,H)	ن	-0.92918	-0.92918	0	0	-153,47405	17716.0	0.81549	-16.68411	-16.49325	84,49	15.26	44.47	1,08953	0.07833
$C_s = (H)C_s - N_s = C_s$	۲,	-0.46459	-1.13380	0 .	0	\$0712.621-	122120	0.82840	-16.42414	-16.23377	90.36	\$9.64	42.49	1,34547	0.00527
$C_{\star} = (H)C_{\star} - N_{\kappa} = C_{\star}$	۸,	-0.46459	-0.92918	0	0		0.93084	0.83885	-16.21953		21,12	19'11	43.14	133135	0.01939
$C_{\mu} = C_{\mu}(H)N_{\mu} = C_{\mu}$	C,	-1.13380	-0.46459	0	0	20712.621-	0.91778	0.82840	-16.42414	-16.23327	137,64	42.16	61.49	0.69250	0.61213
$HN_{,C_{,s}} = C_{,s}(H)$	Ċ.	-1.13380	-0.92918	0 .	0	-153.67867	0.91771	0.80361	-16.88873	-16.69786	136.75	43.25	60,35	0.71784	0.58678
$C_{i}(H)N_{i}-C_{i}=C_{i}(H)$	ن:	-1.13380	-0.92918	0	0	-153,67867	0,91771	0.80561	-16.88873	-16.69786	138.54	41.46	60'19	0.69238	0.60376
$C_{r}(H)N_{s}-C_{s}=C_{s}(H)$	≥,	-0.92918	-0.92918	0	0		0 93084	0.81549	-16.68411		131,92	41.03	65.19	0.63147	0.61467
$N-H(N_oH)$	2,	-0.72918	-0.92918	0	0		0 93084	0.81549	1198991-		117.34	9979	06.29	0.56678	0.37456
$(H)C_{c} - N_{c}C_{s} = C_{s}(H)$	ن	-0.92918	-0.92918	0	0	-153,47405	17716.0	0.81549	-16.68411	-16.49325	138.92	41.08	65.19	£+189°0	0.61467
$C_{\mu} = (H)C_{\mu}N_{\nu} = C_{\nu}$		-0.02918	-0.92918	0	0	-153.47405	Q.91771	0.81549	-16.68411	-16.49325	137,31	6975	26'09	97701'0	86665.0
$C_{s} = (H)C_{s}N_{s} = C_{s}$, v,	-0.02918	-0.46459	0	0		0.93084	.0.83885	-16 21933		138.20	41.80	62.08	67849	0.62534

lable 13,285. The energy parameters (eV) of functional groups of imidazole.	ers (ev) or rundio	Tal mounts of imital				
Farunclers	C = C Group	N = C Group	C.∼ Group	Group	Group	CH Group
'n	2	2	1	2	-	-
η,	0	0	O	0	0	٥
n,	0	0	0	0	0	0
C	0.5	5.0	5.0	20	0.75	0.75
ن	0.85252	0.85252	-	0.85252	0.93613	_
5	1	1	1	7	0.75	
¢,	0.85252	0.84665	0.84665	0.84665	17126.0	0.91771
ć,	0	0	0	0	1	1
<i>c</i> ,	4	7	2	4	-	
5	0	0	0	0	~	_
C.,	0.5	0.5	5.0	2.0	0.75	0.75
<i>C</i> 3.	0.85252	0.83252	-	0.85252	1	
V, (cV)	-104.37986	-103.92756	-32.44864	-106,58684	-39.48897	.39.09538
V, (cV)	20.85777	20,87050	10.07285	20.99432	14,45367	13.45505
T (eV)	35.96751	35.85539	8.89248	37.21047	15.86820	12.74462
V, (cV)	-17.98376	-17,92770	-4,44624	-18,60523	-7,93410	-6.37231
E(2010) (UV)	0	0	-14,63489	0	-14.53414	-14.63489
DE nos to to to to	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
Er[mu] (eV)	2.26759	1.85836	-13.70571	3.71673	-14,53414	-12.36731
Er(420) (cV)	-63.27075	-63.27100	-31.63527	-63,27056	-31.63534	-31.63533
$E_T(alom - alom, msp', AO)$ (cV)	-2.26759	.1,85836	-0.92918	-3.71673	0	
$E_{\nu}(\mathbf{m})$ (cV)	-65.53833	-65,12910	-32.56455	-66.98746	-31.63537	-31.63537
Φ (10 th rad / x)	15.4421	15.4704	21.5213	15.7474	48.7771	28.9084
$E_{\kappa}(uV)$	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
\vec{E}_D (aV)	-0.20668	-0.20558	-0.24248	-0.21333	-0.35462	-0.27301
Erm (aV)	0.17897	0,20768	0.12944	0,11159	0.40696	0.39427
i, (cV)	-0.11720	-0.10174	-0.17775	-0.15754	-0.15115	-0.07587
E. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er(terns) (cV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
Emmy k. in no) (aV)	-14.63489	-14.63489	-14,63489	-14.63489	-14.53414	-14,63489
Emm leg . 10 110) (CV)	0	٥	0	0	-13.59844	-13.59844
Entired (eV)	7.23317	6.79303	3.47253	8,76298	3.51208	3.32988
				:		

values Z	Relative Error	
ed to the experimental	Experimental Total Bond Energy	
13.288 compar	Calcutated Total Bond	
nergies of Table	E.	
sition and the es	HN	
стопр сопра	C-N-C	
g file functiona	C-N	
calculated usin	N=C	
s of imidazole)=)	
The total bond energie	Formula Name C=C N=C C-N-C NH CH Chokkee Experimenal Relative	
Table 15.289.	Formula	

		78					, ,	, ,	_	_80	7			
Exp. θ	117.4 (imidazole)	136,3 (imidazole)	122.9 (imidazole)	136.3 (imidazole)	133.2 (imidazole)	115.8 (fmidazole)	1 10.4 (firridazole)	138.2 (midazole)	129.1 (imidazole)	106.3 (midzzale)	107.2 (imidazole)	105.4 (imidazole)	109.8 (imidazele)	CH1.
(aj. <i>b</i>	120.51	132.86	120,37	135,30	134.28	114,54	112.37	137.80	129.96	107.52	109.83	108.64	111.18	109.80
		106.63				111.18		109.83						
e ©		120.51				134.28		112.37						
e, ©														
Ε _τ	0		٥	0	o				0	-1.44915	-1,85836	-1.85836	-1.85836	-1,44915
'	1.00435		0.97433	961201	1.07647		59296'0		1,01912	0.82131	0.76360	0.77247	0.84958	0.82717
6	0.75		0.73	0.75	82.0		0.75		0.75	-	-	-	-	-
೮	-		-	-	-		-		1	1	-	1	-	-
<u> </u>	6.73		0.75	6.75	21.0		67.0		0,75	-	1	1	-	-
About 2	0.92171 Eq. (15.151))		0.82493 (Eq. (13.64))	0.86359	17716.0		0.84665 (Eq.		0.86284 (Eq. (15.64))	0.79597	0.76360	0,77347	0.14665 (Eq. (15.152))	0,83885
C ₁	1771670		0.84665 (Eq. (15.151))	0.80561	0.85252		0.87499		0.84663 (Eq. (15.151))	0.84665 (Eq. (15.152))	0,76360	0.77247	0.85252	0.81549
Atom 2 Hybridization Designation (Table 15.3R)	2		n		-		z		٥	=	35	25	z	80
Aism 1	-14.53414		-16.49325	-15.75493 C.	-14.82575 .0,		-14.53414		-15.76868	-17.09334 C,	17.81791	-17.61330	-14.53414	-16.21953
Atom I Hybridization Designation (Table 13.3B)	-		z	51	•		•		z	z	36	23	9	2
Eraban Men I	-(4.82575		-14.53414	-16.68873 C.	-15,93954 C,		-15,95954		-14,53414	-14,53414	16118,71-	-17,61330	15,95955	-16.68411
2c' Terroinal Atoms (a _o)	4.0166		3.8987	4,2895	4.2740		3.847!		4.0661	4.1952	4,2426	4,3128	4,3818	4.2544
2c' Ubrad 2 (a,)	2.59228		2.59228	2,60925	2,60925		2.59228		2.5922	2.60925	2.59228	2,70148	2.70148	2.60766
2¢' Bend I (a _e)	2.01241		1.88268	2,02341	2,02241		202241		1.81268	2.59228	2.59228	260756	2,609.25	2 59228
Asun of Arth	ZHC:"N"	ZG,C,H,	".J"NH7	,2,7,42,	ZH,C,C,	ZN,C,H,	ZH,C,N,	ZW,C; H,	ZHN,C,	<i>אונ'נ</i> י	ZC,N,C,	70"M"C"	7C.C.N,	CNCN

PYRIDINE

Pyridine has the formula C_5H_5N and comprises the benzene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in the 5 Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine $C2sp^3$ HO initially has four unpaired electrons. Each C-H bond has two paired electrons with one donated from the H AO and the other from the $C2sp^3$ HO. In pyridine the three N2p electrons are donated to the aromatic bond. Thus, as in the case of the C=C group, each C=N bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the $C2sp^3$ HO and the N2p AO of the participating carbon and nitrogen atoms, respectively.

The solution of the C=N functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single $2sp^3$ shell as an energy minimum, and the sharing of electrons between the $C2sp^3$ HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The C=N-bond MO is solved as a double bond with $n_1=2$ in Eqs. (15.42) and (15.147). The hybridization factor $c_2(C2sp^3HO\ to\ N)=0.91140$ (Eq. (15.116)) matches the double-bond character of the C=N-bond MO is and C_2 and C_2 in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic $C2sp^3$ HO such that $\Delta E_{H_1MO}(AO/HO)=0$ in Eq. (15.42). Furthermore, $E_T(atom-atom,msp^3.AO)$ of the C=N-bond MO in Eq. (15.147) due to the charge donation from the C and N atoms to the MO is $-1.44915\ eV$ corresponding to an energy contribution from each atom that is equivalent to that of an independent methyl group, $-0.72457\ eV$ (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic $E_T(crosp)$ and $E_D(crosp)$ are

given by Eqs. (15.146) and (15.147), respectively, with $f_1 = 0.75$. The breakage of the *CNC* bonds results in three unpaired electrons on the N atom. Thus, the corresponding E_{mag} given by Eq. (15.60) was normalized for the two bonds per atom and for $f_1 = 0.75$ and was subtracted from the total energy of the C=N-bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), 10 (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

15

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_a = N$	C = N

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(aiom – atom, insp³.,
1.7
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35
3. The MO to HO intercept geometrical bond parameters of pyridine. $ \mathcal{E}_{p} $
2
Table 15.293. T
Table

isole 13.293. The MU to MU intercept geometrical bond parameters of pyridine. k_r is $L_r(alnm-alam,msp',AO)$	nernem bonc														
Bond	Atom	(e _X ,	(e V.	E,	E,	Final Total Energy	, sad	, American	$\mathcal{E}_{cons}(C2\mu^2)$	$E(C2:p^3)$	ره)	9.0	ι _θ	, q	d,
,		Bond 1	Bond 2	Bond 3	Bond 4	(23.p)	Ĉ,	(°)	Fina	Final	2	2	2	(°°)	(%)
C-H (C,H)	ن	-0.54343	-0.85035	0.36690	0	-133.57636	17710	0.81052	-16.78642	-16.39556	76.35	103.65	40.11	1,22423	0.19124
C-H (C,H)	ij	-0.85035	-0.85035	-0.56690	0	-(53,88327	0.91771	0.99597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0,21379
(H)C,(H)C,=MC,	U*	-0.85035	-0.54343	-0.56690	0	153,57616	17716.0	0.81052	-16,78642	95565.91-	128.54	51,46	58.65	0.76572	0.50501
$(H)C_{s}(H)C_{s}=MC_{s}$	2	-0.54343	-0.54343	0	0		0.93084	0.85503	15.91261		(30.6)	49.39	60.97	0.71418	0.55656
$(H)C_{s}^{r}=C_{s}(H)N$	ر.	-0 54343	-0.85035	-0.56690	0	-153.57636	17716,0	0.81052	-16.78542	-16.59556	134.85	45.15	59.72	0.74304	0.57165
$(H)_{C_{\mu}} = C_{\mu}(H)_{N}$ $(H)_{C_{\mu}} = C_{\mu}(H)_{C_{\mu}}(H)$	ٺ	-0.85035	-0.85033	-0.36690	0	72:88:251	17716.0	0.79397	-17.09134	-16.90248	134.24	45,76	51.98	0.75935	0.53533

810

Table 15.294. The energy parameters (eV) of functional groups of pyridine	eV) of functional groups	of pyridine.	
Parameters	ر د د		C=N
	Cronb	Cronb	Group
	00	~	0.75
<u>"</u>	2	-	2
n_3	С	0	0
u)	0	0	0
Ü	0.5	0.75	0.5
C.	0.85252	-	0.91140
ប់	1	_	-
5	0.85252	0.91771	0.91140
۲.	0	_	0
ر.'	3	_	3
່ນ	0	-	0
(;·	0.5	0.75	0.5
•.'	0.85252	_	0.91140
V, (eV)	-101.12679	-37.10024	-102.01431
V, (uV)	20.69825	13,17125	21.41410
T(aV)	34.31559	11.58941	34.65890
/, (cV)	-17.15779	-5.79470	-17.32945
E(m.m) (eV)	0	-14.63489	0
Δε _{11,317} (.m m) (αV)	0	-1.13379	0
1: (x) (m) (cV)	0	-13.50110	0
Z_((1,10) (eV)	-63,27075	-31,63539	-63.27076
f.r (dom - alom, my AO) (aV)	-2.26759	-0.56690	-1.44915
(1/2) (aV)	-65.53833	-32,20226	-64.71988
w (10'' rad / s)	49.7272	26.4826	43.6311
E_{κ} (cV)	32,73133	17,43132	28.71875
E_{ν} (aV)	-0,35806	-0.26130	-0.33540
Ex. (aV)	0.19649	0.35532 Fo (13.459)	0.19649
En (cV)	-0.25982	-0.08364	-0.23715
$E_{n_{\mathbf{k}}}(\sigma V)$	0.1480.3	0.14803	0.09457
Ly () (cV)	-49.54347	-32,28590	48.82472
15, may (c. 10) (c/)	-14.63489	-14,63489	-14,63489
Garage le et int (ceV)	0	-13.59844	0
1: n (though (OV)	5.63881	3.90454	4,92005

5.294 compared to the experimental unique [7]	Polyting Energy	: '
gies of Table	Experimental Total Bond France	(eV)
mposition and the ener	Calculated Total Bond Energy	(eV) S1.91802
tional group ∞	CEN	Group
using the func	н.)	5
pyridine calculated	ن در در	
The total bond energies of	Name	Pyridine
Table 15.295.	Formula	CHIN

Table 15.296. The bond angle parameters of pyridine and experimental values [1]. E is E. (atom - atom may 40)	gle paraner	ers of pyric	dine and c	xperimental	values [1]. E. is	E. (atom – at	00, 110, 40)			ì									
אושני נו איבור.	2c' fresi (a,)	2c' line 2 (a ₀)	2c' Tornisel Alone (a,)	Frank Aim I	Atom 1 Hydridization Designation (Table 15.3B)	Franch Akm 2	Atom 2 Hybridization Designation	C ₂	C ₁	ť	5	'u'	ড	E _r (eV)	0, ①	e . O	0, O	Cal. <i>θ</i>	Exp. θ (°)
ZCX.Y' (aromatic)	2,62936	2,62936 4,5385		-17.17218	20	-17,17218	20	0.79132	0.79232	-	-		0.79232	-1.85836		_		120,19	120 [50-32] (benzene) 118.3 (pyridne)
ZCCH (aromatic)											 	1.				9	_		(pyridine) (20 (50-52) (benzene)
ZHC.N	2,06.598	2 54 47 1 9407		14 63576	-				0.91140			+					-	16,611	121.3 (pyridine)
				C C C C C C C C C C C C C C C C C C C	-	-14.334[4	z	17716.0	Eq. (15.116))	6.73	-	0.75	a.99312	0		_		117.65	115.9 (pyridire)
ZWC_C.	2,54147	2.62936 4.5607 -14.53414	4.5607	-14.53414	z	-10.32044	12	Eq. (15)	0.82327	_			0.86734	-1,44913	T	-	F	72 127	123.9
ZY.,M'',	2.54147	2.54147	4,3359	-17.71560	2	-17.71360	2	0.76801	0.76801	-	-	-	0.77601	,2000	\dagger	+	+		(pyridina)

PYRIMIDINE

Pyrimidine has the formula $C_4H_4N_2$ and comprises the pyridine molecule with one additional CH group replaced by a nitrogen atom which gives rise to a second C=N functional group that is equivalent to that of pyridine given in the corresponding section. The 5 aromatic C=C and C-H functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_{a,b,d} = N$	C = N

	<u> </u>	·	т	_	·		· ·
ntal values [1]	Ça.v Smin	1.47169	1.27073	1.34489	1.340 (pyrinidine)	0.74237	27590
pyrimidine and experime	C.H Group	1.60061	1.03299	1.09327	1.084 (pyridine)	1,22265	0.64537
Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1]	C=C Group	1.47348	1.31468	1,39140	1.393 (pyrimidine)	0.66540	0.89223
Table 15.298. The geon	Parameter	a (a,)	c' (a ₀)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a,)	υ

	1		- 1	- 1			1	1				
	9	· ©		101.73	103.65	105.58	\$1.46	4939	\$0.74	49,39	43.76	45.15
	·ø	. C		18.27	76.35	74.42	13.54	130.61	129.26	13061	134.34	134.85
	(6.0)3	(csy)	300	-10.28804	-16,59556	-16.90248	-16.59555		-16.28865		-16.90248	-16.59556
	(520)	(cV) Final	13027731	104/5/01-	-16.78642	-17.09334	-16.78642	15.91261	-16.47951	-15.91261	-17.09334	-16.78642
	13		59569		0.81052	76267.0	0.81052	0.85503	0.82562	0.85503	0.79597	0.81052
		(°)	12100		0.91771	0.91771	0,91771	0.93024	17716.0	0.93084	17710.0	17716,0
	Final Total	Energy C2sp ³	(eV)		-153.57636	-(53.88327	-(33,57636		-153,26945		-153.88377	-153,57636
tom, msp. AO)	E,	(eV) Bond 4	٥		0	0	0	9		c	0	0
is Er (atom-a	Er	(eV) Bond 3	0699\$ D-		-0.56630	-0.36690	-0.56690	0	06995 0-	0	-0.56690	0.55690
syrimidine. Er	B,	(eV) Bond 2	-0 54143		-0.83033	-0.85035	-0 54343	-0.5434J	-0.54343	-0.54343	-0.85035	-0 54343
parameters of p	R_7	(eV) Bond f	-0 (4343		-0,34343	-0.85035	-0.85035	-0.54343	-0 54343	-0.54343	-0.85035	-0.85035
metrical bon	Atom		į,	2.	. ⁷	ن	ਹ ਹ	ຊ້ ຊ້	ن.	* * *	·	ਹ ਹ
faute 13.237. The WIO to the intercept geometrical bond parameters of pyrimidine. E_T is $E_T(atom-atom,msp^2,AO)$	Bond		C-H (C,H)	(= H (C. H)	(1564)	C-H (C,H)	$(H)c_r(H)c_s = N_sc_s$ $(H)c_r(H)c_s = N_sc_s$	$(H)C_r(H)C_s = N_rC_s$ $(H)C_r(H)C_s = N_rC_s$	$(H)C_{s}(H)C_{s}N_{s}=C_{s}(H)$ $(H)C_{s}(H)C_{s}N_{s}=C_{s}(H)$	$(H)C_r(H)C_rN_r\stackrel{a}{=}C_r(H)$ $(H)C_r(H)C_rN_r\stackrel{a}{=}C_r(H)$	$N_{\alpha}(H)C_{s}\stackrel{>}{=}C_{s}(H)C_{s}$ $N_{s}(H)C_{s}\stackrel{>}{=}C_{s}(H)C_{s}$	$N_{\mu}(H)C_{\mu} = C_{\mu}(H)C_{\mu}$ $N_{\mu}(H)C_{\mu} = C_{\mu}(H)C_{\mu}$

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0.55656

60.97

60.97

\$8.98

59.72

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Table 15.300. The energy parameters (eV) of functional groups of pyrimidine.	V) of functional groups of a	pyrimidine.	
Parameters	C Street	C:H Group	C K
7,	0.75		0.75
, L	2		2
1,1	0	0	0
i i	0	0	0
[5]	6.0	0.75	5.0
<i>C</i> ₃	0.85252	ı	0.91140
5	1		1
د,	0.85252	0.91771	0.91140
c,	0	1	0
<i>c</i> ,	3	1	3
c,	0	1.	0
ر!^	0.5	0.75	5'0
ن	0.85252		05116'0
V, (eV)	-101,12679	-37,10024	-102.01431
V, (uV)	20.69825	13.17125	21.41410
7 (0V)	34.31559	11,58941	34.65890
V, (eV)	-17.15779	-5.79470	-17.32945
E(.0 m) (cV)	0	-14,63489	0
ΔΕ _{11,110} (.r. 110) (eV)	0	-1.13379	0
E, [.w.m] (eV)	0	-13.50110	0
E, (n,10) (aV)	-63.27075	-31,63539	-63.27076
$I_T \left(alom - alom, alsp^3. AO \right) (aV)$	-2.26759	-0.56690	-1,44915
$\mathcal{L}_{\mathbf{r}}[\mathrm{ind}]$ (4 V)	-65.53833	-32.20226	-64.71988
ω (101, rad (s)	49.7272	26.4826	43.6311
E_{κ} (eV)	32.73133	17.43132	28.71875
<u>Γ</u> , (αV)	-0.35806	-0.26130	-0.33540
Ban (aV)	0,19649	0.35532 Fo (13.458)	0.19649
E (aV)	-0.25982	-0.08364	-0.23715
Ema (cV)	0.14803	0.14803	0.09457
F. (Grey) (CV)	-49.54347	-32.28590	-48.82472
Frank (c. so no) (cV)	-14.63489	-14.63489	-14.63489
Em (a. 10 m) (aV)	0	-13.59844	0
$E_{ij}(i)$ (cV)	5.63881	3,90454	4.92005

the experimental values [2]. 1.			
300 compared to	Relative Error		-0,00125
mergies of Table 15	Experimental Total Bond Energy	(6V)	46,51794
omposition and the c	Calculated Total Bond Energy	<u>Ş</u>	46.57597
functional group c		dnos	•
ated using the	H.)		•
s of pyrimidine calcu	ر د د د		
he fotal bond energie	Name		rymmicane
1 ADIC 13 301.	Formula	1112	CHILLIAN TO THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PARTY OF THE PA

Absent of Amile	1																		
	26. (a,)	26. bad2 (0,)	2c' Terminal Aleyas (a,)	Lineante Alon f	Atom I Hybridization Designation (Table 15.3B)	Errahat Aten 1	Atom 2 Hybridization Designation (Table 15.3B)	C ₁	C ₁	ָ <u></u> י	ប៉	u-	26	ξ. (eV)	e, ()	0,0	e, ©	(S. E.	Exp. 8
Z(Y.(' (aromaric)	1.62936		4.5365	1,62936 4,5385 -(7,17218		-17,17218	50	0.79232	0.79232	-	-	-	0.797.2	-1.83836		 	 	130.19	(120 [50-52] (beazene) (18.3 (pyridine) 118.5
ZCT 'H (eromatic)	·															61.021	1	19.91	(byndins) 120 (50-52) (benzene) 121.3
ZHCN	2,06598	2,0659\$ 2,54147 3,9497	1,9497	-14.82575	-	-14.53414	z	17716.0	0.9(140 Eq. (13.116)	0.75	-	0.75	0.99312	0	1	+	T	117.65	(pyridine) 115.9 (pyridine)
ZNC:C	2,54147		2,62936 4,5607	-14.53414	z	-16.52644	£1	0.91140 Eq. (15.116))	0.12327	-	-	·-	0.86734	-1.44915		 		123.76	123.9 (byridine)
לכאל.	2.54147	2,54(47	43359	-17.71560	22	-17.71560	z	0.76801	0.76801	-	-	-	0.76801	-1.85836	1	\vdash	1	17.89	115.5
ZNC:N	254147	2,54147	4.5826 -15,55033	-15.55033	^	-(5,55033	-	0.87405	297409	-	-	-	307.00		1	+	+	+	(pyrimidins)

PYRAZINE

Pyrazine has the formula $C_4H_4N_2$ and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The C=N functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic C=C and C-H functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol	
CC (aromatic bond)	C = C	
CH (aromatic)	СН	
$C_a = N$	C = N	

ſ	· 						٦
I values !!	C = N Group	1.47169	1.27073	1.34489	1.403 (pyrazáne)	0,74237	0.86345
Table 14 104 The recometrical bond parameters of pyrazine and experimental values [1]	CH Group	1,60061	1.03299	1.09327	1,115 (pyrazine)	1,22265	0.64537
emical bond parameters of	C=C Green	1,47348	131468	1.39140	1.339 (pyrazine)	0.66540	0.89223
Table 15 304 The renm	Parameter	0 (0,)	c. (a,)	Bond Leugh 2c' (A)	Exp. Bond Length	h,c (a,)	

T-LL 15 105 The MO to HO intercent groungitical bond parameters of pyrazine.	etrical bond	1 paranelers of p	yrazine. E, is	E, is E, (atom - atom, msp3.40).	.msp3.40).								,	-	-
Bond	Atoin	E _r (eV)	Er (eV) Bond 2	(eV) Bond 3	E, (eV) Bond 4	Final Total Energy C2xp*	(0°)	(%)	Er_ (C2rp') (eV) Final	$\begin{bmatrix} E(C2sp^2) \\ (eV) \\ Final \end{bmatrix}$. ₆ ©	θ ⁻ ©	e ©	(a°)	(a _o)
						8						103.66	1.6	1 22423	0.19124
		.0.54343	-0.85035	-0.56590	٥	-153.57636	11716.0	0,81052	-16.78642	-16.59536	cr o/	103.03			
(0,0) 210		1000	0.54143	08998 0-	٥	-153,57636	17716.0	0.81052	-16.78642	-16.59536	128.54	51,46	58.65	0,76572	0.50501
$(H)C_s(H)C_s=NC_s$	٠,	-0.450J	200000						1					31,120	959550
S. C. C.	2	-0,54343	-0.54343	0	0		0.93084	0.8580	-15.91261		19.01	49.19	76,00	T/IGH.	Xacco .
(H)C.(H)C.=NC.											-	• • • • • • • • • • • • • • • • • • • •	÷	0 24304	0.57763
N(H) (H)	ن	-0.85035	-0.54343	0.56690	۰	-153.57636	17/16.0	0.81052	-16.78642	-16,39336	134.85	21.6			
N(11) C. = C. (11) N															

Table 15.306. The energy parameters (eV) of functional groups of pyrazine	eV) of functional groups of	pyrazine.	
Parameters	ڻ ڻڊ		C=N
	Group	Group	Group
γ''	0.75	-	52:0
עי	2	_	2
$u^{\mathbf{r}}$	0	0	٥
<i>n</i> ₁	0	o	0
ن	5'0	0.75	0.5
Ċ,	0.85252	_	0.91140
¢.	-	-	_
c,	0.85252	0.91771	0.91140
5	0		0
ر"	3	1	3
້ວ	0	-	٥
C.	0.5	0.75	0.5
C ₂ ,	0.85252	-	0.91140
V, (eV)	-101.12679	-37,10024	-102,01431
V _r (eV)	20.69825	13.17125	21.41410
T (eV)	34,31559	11,58941	34.65890
V, (cV)	-17.15779	-5.79470	-17.32945
E(w m) (aV)	0	-14,63489	0
DEning (and (al)	0	-1.13379	0
67 (no no) (aV)	0	-13,50110	0
$E_r(u,\omega)$ (cV)	-63.27075	-31.63539	-63.27076
$E_T\{alim - alom, msp^*, AO\}$ (aV)	-2.26759	-0.56690	-1.44915
Erinh (UV)	-65.53833	-32.20226	-64.71988
(10, rad (s)	49.7272	26,4826	43,6311
$E_{\mathcal{F}}(vV)$	32,73133	17,43132	28.71875
E, (cV)	-0.35806	-0.26130	-0.33540
Bra (aV)	0,19649	0.3532 Eq (13.458)	0.19649
Ē., (oV)	-0.25982	-0.08364	-0,23715
E_{mq} (aV)	0.14803	0.14803	0.09457
E, (timp) (cV)	-49.54347	-32.28590	-48.82472
E sand (r. 101111) (cV)	-14,63489	-14.63489	-14.63489
Guerale, it in) (aV)	0	-13.59844	0
1: plome (cV)	5.63881	3.90454	4.92005

: experimental values [2	
6 compared to the Relative Error	
pres of Table 15.30 Experimental Total Bond Energy	
Iposition and the energy Calculated Total Bond Energy	5
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led using the fun	
yrazne calcular C.*C	
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26936 4.588 -17.17218 20 0.77232 0.79232 -1.18836 -1.18836 2.06379 2.06379 2.26379 2.26379 2.264147 3.9677 -1.48316 N 0.91140 0.91140 0.9757 1 0.7723 -1.18836 1 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.19 19.		(a)	(o,)	Transmet Aliense (a)	Land A	Atom I Hybridization Designation (Table 15.38)	Aim 2	Atom 2 Hybridization Designation (Table 18 19)	C ₂	C ₂	ບັ	Մ	٠.	ۍ.	E, (eV)	0°. ©	9 0		al. <i>θ</i>	Exp. 8
2.06594 2.54147 2.52946 4.045 -14.53414 N -17.0934 7 -18.00 1	ACCC (aromatic)	2,62936	2.62936	4,5585	-17,17218	R	-17,17218	20	0.79232	0.19232	-	-	-	0.79232	-1.85816			+	61.09	120 [50-52] (henzene) 118.3 (pyridine)
2.06592 2.54147 3.9497 -14.82575 1 -14.33414 N Q.91771 Eq. 0.75 0.99112 0 120.19 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11765 116.81 11	".Cu										1						_			118.5 (evridies)
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1765 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681 1681	14.217									071100	1								_	frondine)
2.34147 2.52196 4.4045 1.1731560 24 -1771560 24 -1771560 24 0.76801 0.76801 1 1 0.76801 1.183336 1.183336	אין אין	7,00391	234167	3.9497	-14.82575	_	-14.53414	z	0,91771	ם	0.73	-	0.73	0.99312	0		-	-	-	115.9
234147 2.54147 4.3359 -1.771540 24 -1.771540 24 0.76801 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 1 0.76801 1 0.76801 1 0.76801 1 1 0.76801 1 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76801 1 0.76	ZCCH									(15.116))	1		†						60',	(pyridine)
2.54147 2.52196 4.4045 -14.51940 24 -17.71560 24 0.75610 1 1 1 0.75610 -1.83506 -1.83506 -1.83506 -1.83506 -1.83506									- 1	1			-						5.54	1239
2.54147 2.54147 4.3359 -17.71560 24 -17.71560 24 0.76801 1 1 1 0.76801 1 1 0.76801 1.83836	ZWCC	2.54147	2.62936		-14.53414	z	-17.09334	•	Eq.	0.79597	_	-	-	0.85368	-1.44915	┢	-	F		(pyrazne) 115.6
24 0.76801 1 1 0.76801 1.183336	ZY.W.	2,54147	2.54(47	4.3359	035 17 7 1 5 60	7.	13.15.0		i i	1		1					_	-		(pyrazine
_						:	-17.71500	77	0.76801	0.76801		_	<u>-</u>	0.76801	-1.85836			L=	117.09	116.8

QUINOLINE

Quinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. The aromatic C=C and C-H functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic. The C-C functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the C=N group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	СН
$C_b - C_b$ (bridging bond)	C-C
$C_{u,d} = N$	C=N

Table 15.310. The geom	netrical bond parameters of	Table 15.310. The geometrical bond parameters of quinoline and experimental values [1].	al values [1].	200
Parameter	J Grand	Group	Group	Orong Orong
0 (0°)	1,47348	1.60061	1.75607	1,47169
c. (a,)	1,31468	1.03299	1.32517	1.27073
Bond Length 2c' (A)	1,39140	1.09327	1,40250	1,34489
Exp. Bond Length	1.40 (avg.) (naphthalene)	1.101 (benzena)	1.42 (naphthalene)	1.340 (pyridine)
h,c (a,)	0.66540	1.22265	1.15226	0.74237
	0.80223	0.64537	0.75462	0.86345

Table 15.311. The MO to HO intercept geometrical bond parameters of quinoline. E_r is $E_r(anm-ann,msp^1.AO)$	netrical bon	d parameters of	quinofine. Er i.	s E _r (annn – ann	m, msp³.40).						
Bond	Atom	E,	£,	E_T	E	Final Total	.,	.]	(C24")	$E(C2sp^2)$.6
		(§	(eV)	(e)	(eV)	Energy	(")	(2)	(¢		٥
		Bond i	Bond 2	Bond 3	Bond 4	C24a	È	3)	Final	Final	2
						(§					
(C-H(C,H)	ن'	-0.85035	-0.54343	-0.56690	. 0	-153.57636	17716.0	0.81052	-16.78642	-16.59556	76.35
$C \sim H (C, H)$	C,	-0.85035	-0.15035	-0.56690	0	-153.86327	17716.0	0.79597	-(7.09334	-16,90248	74.42
$N(H)C_s = C_s(H)$	· .	-0.83033	- 0.54343	-0.36690	0	-153.57636	17716.0	0.81052	-16.78642	-16.59556	134.85
$(H)_{C_{s}=C_{abc,s}(H)}$	C,	-0.85035	-0,85035	06995:0-	0	-133,88327	17716.0	0,79397	+17.09334	-16,90248	134.24
$(H)C_{s}(C_{s})C_{s}=C_{s}$	ن	-0.85035	-0.85035	-0.28345	0	-153,59983	17716.0	0.80939	6\$608'91-	-16,61903	134,81
N(c,)c, = c,	C.	-0.85035	-0.54343	-0.28345	o	-153,25292	17719.0	0.82445	16,50298	-16 31211	135.42
$C_{\lambda}(H)C_{\lambda}=N$	C,	-0.85035	-0.34343	-0.36690	0	-153,57636	17716.0	0 81052	-16.78642	-16.59556	128.54
$C_{\lambda}(H)C_{\lambda}^{-s}N$ $C_{\lambda}(C_{\lambda})C_{\lambda}^{-s}N$	<i>N</i>	£}£P\$*0-	-0.54343	0			0.93084	0.83503	-15.91261		130.61
C _k (C,)C,=N	ڻ ت	-0.85035	-0.54343	-0,28345	0	-183,29291	17710.0	0.82445	-16.30297	-16.31211	12821
$\left \left\langle (H)C_{s} \right\rangle \right C_{s} - C_{s}$	υ,	-0.83035	-0.83033	-0.28343	0	-153.59983	17710.0	0.80939	68608'91-	-16.61903	10'56

0.55656

60,97

49.19

45,33

16.31

17716.0

-153,29292

0,74304

45.19

38.84 59.72 58.98

(o) o

6,0

Table 15.312. The energy parameters (aV) of functional groups of quinoline.	V) of functional groups of	quinoline.		
Parameters	ريد Group	C.H. Group	C-C Group	ς. Group
γ.	0.75	-		0.75
$n_{\rm f}$	2	-	1	2
<i>u</i> ,	0	0	Φ	C
H3	0	0	o	0
כ'	0.5	0.75	0.5	0.5
C_{i}	0.85252	-	1	0.91140
5	-	-		-
c,	0.85252	0.91771	0.85252	0,91140
5	0	_	0	0
, c ₄	3	_	7	3
C.3	0	-	0	0
ر.	0.5	0,75	6.5	0.5
2.5	0.85252	-	1	0,91140
V, (aV)	-101.12679	-37,10024	-34,43791	-102.01431
V, (eV)	20.69825	13.17125	10.26723	21,41410
7 (eV)	34,31559	11.58941	9.80539	34.65890
V., (eV)	-17.15779	-5.79470	-4.90270	-17.32945
E(n m) (cV)	0	-14.63489	-14.63489	0
DE u, so (in in) (aV)	0	-1.13379	-1.13379	0
15, (so m) (cV)	0	-13.50110	-13.50110	0
$E_r(n_r\omega)$ (cV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_r(alam - alam, mxp^2, AO)$ (eV)	-2,26759	-0.56690	06995"0-	-1.44915
Er (10) (aV)	-65.53833	-32,20226	-32,20226	-64.71988
w (1013 rad I.S)	49.7272	26.4826	23.6343	43.6311
\vec{E}_{K} (eV)	32.73133	17.43132	15.55648	28.71875
\vec{E}_n (cV)	-0.35806	-0.26130	-0.25127	-0.33540
E 4 (aV)	0.19649	0.35532 Eq. (13.458)	0,12312 [2]	0,19649
1. (eV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{n\sigma}\left(eV ight)$	0.14803	0.14803	0.14803	0.09457
$E_T^{\text{(bound)}}(aV)$	-49.54347	-32,28590	-32.39198	-48.82472
Emma(r, un und) (uV)	-14.63489	-14.63489	-14.63489	-14,63489
Eman (a.10 10) (aV)	0	-13.59844	0	0
$E_{D}(temp)$ (cV)	5.63881	3.90454	3.12220	4.92005

Table 15.313. The total bond energies of quinoline calculated using the functional gro

	E I			(napi	
	Cal. 6		119.40		120.30
	e, ©				
	0 O		_		¥.
	ø, ©	\downarrow			
	E, (eV)		-1.85836		
	ν		0.79232		
lues [2]. J	i,		-		-
lative Error	ບັ		-		
to the exp	5		-		-
1 compared to the experimental v Experimental Total Bood Energy Relative Error (eV) 85.48607 0.00178	C ₂		1000		0.78050 0.76801
Total Band Energy (e.v.) 85,40453	C,	0.1013	200.0		0.78050
une crorges of Calculor (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor) (Calculor	Atom 2 Rybridization Designation	30	:		77
C=N Group 2 2 2 C=N Group 2 C-N C-N C-N C-N C-N C-N C-N C-N C-N C-N	Economic Albert 2	81271.51-			-17.71560
C.H. CI. CI. CI. C. CI. Total Band Energy Total Bond Energy Relative Energy Copy (cv) (cv) (cv) (cv) (cv) (cv) (cv) (cv)	Aton I Hybridization Designation (Table 15.18)	Q2			22
CH 7 experiments	Eratem I	-17.17218			-17.43216
C=C	· 2c' Termand Altern (a _n)	4.5585			4.3818
rs of quin	2c' !kind1 (a,)	2,65034			434147
Name ngle paramete	2c' Hand 1 (a,)	262936 2.65034 4.5585			4.3818
Pomula Name $C = C : H : C = C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : C = M : $		22.27	H.J.J.Z	/C MC	200
3 £			Ц		

ISOQUINOLINE

Isoquinoline has the formula C_9H_7N and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic C=C and C-H functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic. The C-C functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the C=N group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15:317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each $E_D(G_{Tump})$ of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_b - C_b$ (bridging bond)	C-C
$C_{a,d} \stackrel{3\epsilon}{=} N$	C=N

			_				_
	ريم Græip	1.47169	1.27073	1.34489	1.340 (pyridine)	0.74237	0.86345
mtal values [1].	C-C Group	1.75607	1,32517	1.40250	1.42 (naphthalene)	1.15226	0.75462
Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1].	CH Group	190091	1.03299	1,09327	1.101 (benzene)	1,22265	0.64537
etrical bond parameters of	C=C Group	1,47348	1.31468	1,39140	1.40 (avg.) (naphthalene)	0.66540	0.89223
Table 15.316. The geom	Parameter	(%) 0	c. (aº)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (v ₀)	3

					82	6_			ι-
(°p)	0.19124	0.19124	0.21379	0.57165	0.55533	0.57038	0.50501	0.55656	0 0 7066
(°°)	1,22423	1,22423	1,34678	0.74304	0.75935	0.74430	0.76572	0.71418	1.25451
(°)	40.11	40.11	38.14	п.88	58.93	99:65	58.65	60.97	44.41
θ ₁ (°)	103.65	. 103,65	105.58	45.15	45.76	45.19	51.46	49.39	84.99
.) (•)	76.35	76.35	74.42	134.85	134,24	134,81	128.54	130,61	95.01
E(C2sp ³) (eV) Pinal	-16.59556	-16.59556	-16.90248	-16.59556	-16.90248	-16,61903	.16.39536		1661903
Ec. (Cip) (eV) Final	-16.78643	-16.78642	-17,09334	-16.78642	-17,09334	-16.80989	.16.78642	-15.91261	0X608.91
(o,)	0.81052	0.81052	0.79597	0.81052	0.79397	0.80919	25018:0	0.85503	0.809.0
(a)	0.91771	17716.0	0.91771	177180	12719.0	0.91771	0.91771	0 93084	122160
Final Total Energy C2xp³ (eV)	-153.57636	-153.57636	-153.88327	-153,57636	-153,88327	-153,59983	-153.87636		-1 S3 S99R3
Er (eV) Bond 4	0	0	0	0	0	0	o	o	٥
E _r (eV) Bond 3	-0.56690	-0.56690	-0.56690	-0.36690	06995'0-	-0.28345	0.56690	•	-0.28345
E _r (eV) Bond 2	-0.54343	-0.54343	-0.85035	-0.54343	-0.85035	-0.45015	-0,54343	-0.54343	-0.85035
E _r (eV) Bond I	-0.83033	-0.85035	-0.85035	-0.85035	-0.85035	-0,85035	-0.85035	-0.54343	.0.85035
Атоп	ີ່ວ	c,	ڻ	ਦੇ ਹੋ	ن د	6.7	<i>5</i> 5	N	
Bond	C - H (C,H)	C – H (C,H)	C-H (C,H)	N(H)C,=C, N(H)C,=C,	$(H)C_{r}^{\lambda c}=C_{hc,s}(H)$	$(H)C_{\nu}(C_{\nu})C_{\nu}=C_{\nu}$	$C_{\rho}(H)C_{\mu}^{N}$ $C_{\rho}(H)C_{\mu}^{N}$	$C_{\nu}(H)C_{\nu}^{\lambda}=N$ $C_{\nu}(H)C_{\nu}^{\lambda}=N$	C (C)C'-C'

	,,	7.5	., .,	3. 1
Parameters	o diago	Group	Group	v=2 Group
7,	0,75	-	_	0.75
n,	2	-	-	2
n,	0	0	c	0
n,	0	0	0	o
ر:	0.5	51.0	0.5	0.5
رز	0.85252		-	0,91140
5	_	1	-	1
ร์	0.85252	0.91771	0.85252	0,91140
6,	0	1	0	0
6,	3	ı	2	£
ć,	0		o	0
.; .;	0.5	0.75	0.5	0.5
ر.	0.85252	1	-	0.91140
V, (cV)	-101,12679	-37.10024	-34.43791	-102.01431
V, (eV)	20.69825	13,17125	10.26723	21,41410
7 (eV)	34,31559	11,58941	9.80539	34.65890
V. (cV)	-17.15779	-5.79470	-4.90270	-17.32945
E(m m) (aV)	0	-14,63489	-14,63489	0
δΕ 11.34 (20 m) (aV)	0	-1.13379	-1.13379	0
$E_T(x_I m) (cV)$	0	-13,50110	-13.50110	0
$E_r[u_i, u angle](cV)$	-63.27075	-31.63539	-31.63529	-63.27076
$E_r(alam - alam, msp^3, AO)$ (cV)	-2.26759	-0.56690	-0.56690	\$164411-
$E_r(\iota,\sigma)$ (cV)	-65.53833	-32,20226	-32.20226	-64.71988
a (10" rad/s)	49.7272	26.4826	23.6343	43.6311
$E_{K_{c}}(eV)$	32.73133	17.43132	15.55648	28.71875
\widetilde{E}_{Ω} (aV)	-0.35806	-0.26130	-0.25127	-0.33540
Exit (aV)	0.19649	0.35532 Eq. (13.458)	0.12312	0.19649
$ec{E}_{ m pg}\left(cV ight)$	-0.25982	-0.08364	17981.0-	-0.23715
$E_{\rm max}$ (oV)	0.14803	0.14803	0.14803	0.09457
$E_r(i_{r-1})$ (cV)	-49.54347	-32.28590	-32,39198	-48.82472
E (5, 40 HC)	-14.63489	-14,63489	-14,63489	-14,63489
Emay le, wo in) (cV)	0	-13.59844	0	0
Enlime) (aV)	5.63881	3.90454	3.12220	4,92005

sition and the energies of Table 15.318 compared to the experimental values [2].].

1 1	rgy Ketanve Enter		0.00046
alculated Experimental	Total Bond Energy	(%)	85.44358
Calculated	Total Bond Energy	(e _s)	85,40453
	CIIN	Group	-
c Initeriorial Brond	1	Grønp	-
כמומנבם מצווות נוו	7.7	E	-
1 13 Odininoline cal	2.) C	
e total bond encreics o	,	Nanta	
Table 15.319. Th		Formula	

Exp. 6	(•)	119.4	(naphthalene)				
2	ေ		119.40	120.30	0.01		
q	6 ©					1	
,	· (E)			119.40			
·	s) ©	Ī	_				
	(e.y.)		-1.15336		20000	-1.53530	
Ī	٧,		0.79332		ļ	0.77426	
	<u>. </u>		-	Ī	1	-	
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	ڻ ٽ		_	T		_	
	C ₂	1	0.79232		1	0.76801	
	C ₂		0.79233 0.79232	1	1	0.78050 0.76801	
100 (1) 12 14 17 (min)	Arom 1 Hybridization Designation	(Table 15.3B)	82			77	4
	F. Cademon. Alera 2		-17.17218			-17,71560	
101 401000 111.	Atom 1 Hybridization Designation	(Table 15.3B)	Ę	:		,	
יו כאלבנוווביו	12° 2° E. Harrian Ahari Philis	-	1100101	.,,,,,,		Aictaci	
אנה שת ווסת	2c* furnism	(°				1	
1500110	26 18 (a)	-		*CDCO.7			-
. parameters	, i 2c,		1100101	2,62936		ALTHOUGH STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STATE STA	1
e 15 320. The bond angle parameters of isoquinounce and experimental va	Ahres of Angla	_		7,4,5	17.7.77		ZC. MC.

INDOLE

Indole having the formula C_8H_7N comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic $C_-^{3\epsilon}C$ and C-H functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The CH, NH, and $C_d = C_c$ groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The $C_b - C_d$ single bond of aryl carbon to the $C_d = C_c$ bond is also a functional group. This group is equivalent to the C - C(O) group of benzoic acids with regard to $\Delta E_{H_1MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) both being -1.29147 eV. This energy is a linear combination of $\frac{-1.13379 \text{ eV}}{2}$, $E_T(atom-atom,msp^3.AO)$ of the C-H group that the $C_b - C_d$ and C - C(O) groups replace, and that of an independent $C2sp^3$ HO, -0.72457 eV (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term c_2 is the aromatic $c_2(benzeneC2sp^3HO) = 0.85252$ to match the aryl $C2sp^3$ HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with $n_1 = 2$ in Eqs. (15.42) and (15.52). The hybridization factor $c_2(arylC2sp^3HO\ to\ N) = 0.84665$ (Eq. 20 (15.152)) matches the aromatic character of the $C2sp^3$ HOs to the N atom of the NH group, and C_2 and C_{2n} in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143), $C_2(benzeneC2sp^3HO) = 0.85252$. Furthermore, $\Delta E_{H,MO}(AO/HO)$ in Eq. (15.42) and $E_T(atom-atom,msp^3.AO)$ in Eq. (15.52) are both $-2.42526\ eV$ which is a linear combination of $\frac{-1.13379\ eV}{2}$, $E_T(atom-atom,msp^3.AO)$ of the C-H group that the 25 C_c-N bond replaces, and $-1.85836\ eV$ (Eq. (14.513)) which is equivalent to the corresponding component of the C-N-C-bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each $E_D(Group)$ of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	C = C
$C_b - C_d$	C-C
CH	CH (ii)
$C_c - N - C_e$	C-N-C
NH group	NH

Table 15.322. The	e reometrical bond paran	Table 15.322. The geometrical bond parameters of indole and experimental values [1]	inental values [1].					
Parameter	ن الم الم	C.H. (i) Group	C ≈ C Group	('H' (ii) Group	C ~ C Group	C−N−C Grœup	NH Group	
a (a _o)	1.47348	1,60061	1.45103	1.53380	1,81395	1,44394	1.24428	
c. (a,)	1.31468	1.03299	1,30463	1.01120	1.34683	1.30144	0.94134	
Bond Length 2c' (A)	1.39140	1.09327	92086.1	1.07021	1,42542	1.37738	0,996270	
Exp. Bond Length (A)	1.399 (benzene)	1.101 (benzene)	1.382 (pyrrole)	1.076 (pyrrole	1.417 (pyrrole)	1.370 (рупоlе)	0.996 (pyrrole)	
h,c (a,)	0.66540	1,22265	0.63517	1.15326	1,21510	0,62548	0.81370	
3	0.89223	0.64537	0.89910	0.65928	0.74248	0.90131	0.75653	

<u>ا</u> څ	ical bond	Table 15.323. The MO to HO intercept geometrical bond parameters of indole. R_1	22						-						
Atom		E,	li,	. Er	E.	Final Total]		(Chr.)	E (C.25p')	ib	6 5	Φ,	7	, e.
		(cV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	('2.5p)	(a,)	(a)	(eV) Final	(eV) Final	(•)	(0)	(.)	(%)	(°)
٠٠	r	-0.85035	-0.85035	0.36690	0	155,84327	0.91771	0.79397	-17.09334	-16.90248	74.42	105.58	38.84	1,24678	0,21379
ئن	1	-0.85035	5 60 58 0-	-0.56690	0	72638,661.	177160	0,79397	-17,09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533
ن •	1	-0.85035	-0,64574	-0.85035	0	2)2963631-	0.91771	0.79232	.17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124
ن	ı	-0.60631	-0.85035	-0.85035	0	.(53,92270	17716.0	0.79414	-17,13276	-16.94190	134.16	45.84	58.89	0.76140	831
٠	Ц_	-0.85035	-0.85035	-0 64574	С	-153.96212	17716.0	0.79232	-17.17218	-16.98132	87.89	92.11	40,66	1.37597	0.02914
٠٠	ı	-0,64574	-(.13379		c	-153.39522	17716.0	75618.0	-16,60528	-16.41442	90.51	89.49	42.40	1,31953	97.000
ن	L	-0,64574	-1,13379	0	٥	-153.19522	17716.0	0.81937	-16,60528	-16.41442	137.29	42.71	61.04	0,70255	0.60208
٠.	L	,1,13379	-0.60631	•	٥	-153.35580	0.91771	0.82132	-16.56526	.16.37500	137.37	42.63	61.14	0.70038	0.60425
	1	-1.13379	-0.60631	0	0	-153.35580	0.91771	0.82132	-16,56586	-16,37500	138.03	41.97	61.42	0,69030	₩901970
N		-0,60631	-0.60631		0		0.93084	0.84833	16.03838		139.04	40.96	62.76	0.66083	0.64061
2	<u> </u>	-0.60631	16909.0-	0	0		0.93084	0.84833	-16,03138		119.52	60.48	65.13	0,52338	0.41796
٠.	L_	-0.85035	-0.85035	16309.0-	0	69226'851-	17716,0	0.79414	17,13376	-16,94189	136.97	43.03	60.05	0.72095	0.58048
ĺ	l														

Table 15.324. The energy parameters (eV) of functional groups of indole	rs (eV) of functions	d proups of indole	ai.				
Parameters	ن ا ا ا	CH (i) Group	C=C Group	C ~ C Group	CH (ii) Group	C-N-C Group	NH Group
J'	0.75	1	-	-	1	1	1
<i>n</i> ,	2	-	2	1	1	2	-
<i>n</i> ,	0	0	0	0	0	0	0
n,	0	0	o	0	0	0	0
ζ,	0.5	0.75	0.5	0.5	0.75	0.5	0.75
	0.85252	_	0.85252	1	1	0.85252	0.93613
j.	-	1	_	1	1	1	0.75
5	0.85252	0.91771	0.85252	0.85252	17716.0	0.84665	0.92171
· v	0	-	0	0	1	0	1
6,	۴.		P	2	1	4	-
'5	0	-	0	0	-	U	-
	0.5	0.75	6.5	0.5	0.75	5.0	0.75
ۺ	0.85252	1	0.85252	1	7	0.85252	1
F, (cF.)	-101,12679	-37,10024	-104.37986	-32.93291	.39,09538	-104.73877	-39.48897
7, (e.Y.)	20.69825	13.17125	20.85777	10.10210	13.45505	16806'07	14.45367
T (aV)	34.31559	11.58941	35,96751	9.07768	12.74462	36.26840	15.86820
7, (27)	61721,11-	-5.79470	-17.98376	4.53884	-6.37231	-18.13420	-7.93410
1:(.v. m) (eV)	0	-14,63489	0	-14.63489	-14,63489	0	-14.53414
DE High (so m) (cV)	0	-1.13379	-2.26759	-1.29147	-2,26758	-2,42526	0
Er (.r. m) (cV)	0	-13.50110	2.26759	-13,34342	-12,36731	2.42526	-14.53414
Er (und) (cV)	-63,27075	-31.63539	-63.27075	68389'18-	-31.63533	-63,27040	-31.63534
Er (alom - alom, msp. AO) (cV)	-2.26759	-0.56690	-2.26759	-1,29147	0	-2.42526	0
Er(sn) (aV)	-65,53833	-32.20226	-65.53833	-32.92684	-31.63537	-65.69600	-31.63537
(1013 rad/s)	49,7272	26.4826	15.4421	21.8249	28.9084	54.5632	48.7771
$E_{K}(aV)$	32,73133	17.43132	10.16428	14,36554	19.02803	35.91442	32.10594
<u> </u>	-0.35806	-0.26130	-0.20668	-0.24690	-0.27301	-0.38945	-0.35462
Era (cV)	0.19649	0,35532 Fo (13.458)	0.17897	0.12312	0.39427	0.11159	0.40696
Row (cV)	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.33365	-0.15115
E (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E_T (times) (CV)	49.54347	-32.28590	-65.77272	-33.11218	-31.71124	-66,36330	-31.78651
E (c. 1) 10)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,53414
E (9. 10 110) (cV)	0	-13.59844	0	0	-13.59844	0	-13.59844
Entirmy (cV)	5.63881	3.90454	7.23317	3.84240	3.32988	7.82374	3.51208

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Calculated Total Bond Energy	()	78.322.3	1 2 1 2 1		້.		_		
			est erev	3	ن ن		-	İ	
NH	-		dine angle		C ₁ Alam 1		0,79232		
C-N-C	-		om the prece		C ₁		0.79132	†	
CH (ii) C-N-C NH	-		. the parameters fi		-	(14ble (5.1B)	2		
3-3	-		culation of θ		Erateshar Alican 2	1	17.17218	ľ	
J-J C=C () H.			ilues [1]. In the cal			(ac'c; 51081)	29		
CH (I)	4		erimental va		Commercial Average		-17,17218		
ر ا ا	۰		s and exp		2c. Normand Norman (a,)		5		
G			ers of indole		(a) [(a)		71.77		
Name			gle paramet		2c (a _n)	200.5	4.02330		
Pormula P	CrH'N indole		Table 15326. The bond angle purumeters of indole and experimental values [1]. In the calculation of θ , the parameters from the preceding angle were most E is $E \left(\frac{1}{2} \cos \theta \right) = \frac{1}{2} \cos \theta$	Alams of Applic		2,2,27	(aromatic)	H2:37	(aromatic)
٠.'	'			_				_	_

ADENINE

20

Adenine having the formula $C_5H_5N_5$ comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The 5 aromatic C = C, C - H, and C = N functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The NH_2 and $C_a - N_a$ functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The CH, NH, $C_a - N_e$, and $N_e = C_e$ groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The C - N - C functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the C - N - C group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each $E_D(\text{Group})$ of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
$C_{b,c} = N_c \qquad C_{a,b} = N_b$	C = N
$C_a - N_a$	C-N (a)
NH ₂ group	. <i>NH</i> ₂
$N_{\epsilon} = C_{\epsilon}$ double bond	N = C
$C_d - N_e$	C-N (b)
N,H group	NH
СН	CH (ii)
$C_e - N_d - C_e$	C-N-C

	C-N-C Group	1.44394	1.30144	1.37738	1,370 (pyrrole)	0.62548	0.90131
	, s	1.4	1	£.1	- (g)	9.0	5.0
	CH (ii) Greup	1.53380	1.01120	1.07021	1.076 (pyrrole)	1.15326	0.65928
	NH Group	1,24428	0,94134	0.996270	0.996 (pyrrole)	0.81370	0,75653
	C-N (b) Group	1.82450	1.35074	1,42956		1,22650	0.74033
-	. V≃C Group	1.44926	1,30383	1,37991		0.63276	0.89965
	, HW	1.24428	0,94134	0.99627	0,998 (anilina)	0.81370	0,75653
	C-N(a)	1.81158	1.34595	1,42449	1.431 (anilina)	1,21254	0.74297
Terman values	CaN	1.47169	(,27073	1.34489	1,340 (pyramidine)	0.74237	0.86345
me and experi	() #3 29 mg	1.60061	1.03299	1.09327	1.084 (pyridine)	1,22265	0.64537
bie 13,328. The geometrical bond parameters of agent	ن ن د *	1.47348	1.31468	1.39140	1.393 (pyrimidine)	0.66540	0.89223
tole 13,328. The goon	Parameter	0 (0,)	c, (a,)	Bond Langth 2c' (A)	Exp. Bond Length (A)	h,c (a,)	,

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Table 15.319. The MO to HO intercept geometrical band parameters of adenine. R, is an alkyl group and R.R.R. are H or alkyl groups.	cometrical box	nd parameters of	adenine. R is a	n alkyi group an	d R.R.R. are	H or alkyl grot.	105 E, is E, (E_r is $E_T(\alpha tom - \alpha tom, nup^3, AO)$	up'.ΑΟ).						
Bond	Atom	E,	Ę	E,	4	Final Total		.3	(C2.ps)	E(C2sp2)	6	0,	6,	ď	ď,
		(eV) Bond 1	(eV) Bond 2	(eV) Bond J	(cV) Bond 4	Energy C21p ² (eV)	(0,)	(%)	(eV) Final	(eV) Final	0	①	(.)	(a,)	(a,)
C,(N,)C,N,H-H	χ.	0.56690	0	0	0		18060'0	0.88092	15.39265		121,74	58.26	67.49	0.47634	0.46500
C,(N,)c; -N,H,	٠٠٠	0.36690	CrCr5'0+	-0.83035	0	יוטעינגוי-	17716-0	0.81052	-16.78642	95565'91'	06'GR	01.02	41.95	124737	0.00142
C,(N,)C, -N,H,	Σ,	0.555.0-	•	0	c		13060	0.XKD92	.13,39265		96.32	89°CX	46.43	1,24139	0 03736
C-H (C,H)	ت	0.54343	6.9343	06995-0-	0	-153,26945	וידופס	0,82562	16.47951	16.29864	78.27	101.73	41.39	1300%1	0.16783
C-H (C,H)	ان	N1CZ(;0-	-0.60631		o	-153.15110	177160	031550	2,16,36125	-16.17038	79.01	CC'001	41,87	1.19159	0.15860
N-H (N,H)	N	-0.60031	-0,60631	0	0		0.930H	0,84833	16.03138		119.52	27'09	63,13	0.52338	967 170
C,(MH,)C,=N,C,	ť.	S £05X'D+	(rtestr	0095'6	0	153,57036	17710-0	0.81052	-16.78642	9856591-	128,54	97'18	58.65	0.76572	0.50501
C,(NH,)C,=N,C, N,C,=N,C	z z	6,54343	crerso	0	o		PROCEGO	0.8593	1921621.		130.61	61.04	76.09	0.71418	0.35656
N,C, & N,C,C,C, N,C,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,N,C,C,	· ·	a.54343	0.54343	0095 b-	a	-153.26045	17714.0	0 XZ\$G2	-(6,4795)	-16,20063	97.62.1	50.74	#	0.74/24	0.52240
い。(ペル)じールに		40,K40.5	4,54343	1000 n-	0	-153,61578	171100	O.NONG3	-16.82584	16-E3-81	128.45	51.55	38.55	0.76752	0.30281
N, (N, H,)C, "C, (N,)C,	3	-0,88105	41,543,43	06950	0	9(5/5/33)-	17716.0	0,81052	-16.78642	+16.59336	SR+CI	43.13	27.65	0,74304	237163
N,{N,H ₃ }C;=C;{N,}C; C;{N,}C;=C;{N,H}N,	3	-0,4503.5	\$5055.0-	(sትንት 'o-	8	-153,78097	17710.0	0.00076	snice.yi-	-16.80017	1740	95'61-	27.65	0.75398	140950
C, (N,)C, *C, (N,H)N,	<u>ئ</u> ا	SEISK'O-	6,54343	1 (2019) 11+	0	-151,61578	0.91771	D NONC3	-16.823H	46+CV-91-	134.77	43.13	29.65	0.74516	0.56952
C,(N,)C,~N,H	.,	-0 85035	.0.54343	16307.0-	0	-153.6157R	17710.0	D. MONGO	H8524.91-	-16,63.49R	137.54	47.46	87.03	0,70448	0.39636
$C_{\nu}(H)\nu_{\mu} - C_{\nu}(\nu_{\nu})C_{\mu}$ $\nu_{\nu}(H)C_{\nu} - \nu_{\nu}(H)C_{\nu}$	N,	יויניטעינו	18909'0-	U	ð		nko£6.0	0 84(03)	-16.03H3R		139,04	96'01	27.20	0,66040	0,64061
N'(H)c.'-N'(H)c.'		-0.60631	₩17 <u>2</u> 2,0~	Û	0	-133,15119	17710,0	0.83159	-163623	-16.17039	138.42	11.54	61.93	0,679,40	0,62203
$C_{\nu}N_{\nu} = C_{\nu}(H)N_{\nu}H$	·.'	-0,9291¥	163170-	0	ı,	153,15119	177160	081680	-16 36125	-16.17039	137,93	42.07	27.19	0.68657	27190
H'N(H)', J = 'N', J	ν,	-0.9291N	0.46459	0	0		0.93084	0,83883	-16.21932		138.20	03 11	62.08	0.67849	a62334
ינ'(נ')נ'-א'נ'	N,	-0,16.159	-0.9201Ж	ů	0		09308	0.83885	-16.21932		56.19	88.GH	43.34	£5165.1	0.01939
נ.'(נ.')נ.' – א'נ.'	ن	6319117	SEUSKO-	SEOSHU	c	16031,12).	17710,0	0.10076	-16 99 103	-16,80017	x7.71	91.29	10.72	1_3H2R0	003200

7.7		laure 13.330. The criefly parameters (cv / or transmissing property)	·c.							
Parameters	ر الالال الالال	S to	ر الاستان Spaus	C-N (a) Group	NH, Group	N = C Group	C - N (b) Group	NH Group	CH (fi) Group	C-N-C Group
7	0.75	-	0.75	-	-		-		-	1
u u	2	-	2	-	2	2	1	-	-	2
n,	0	0	0	0	0	0	0	0	0	0
n,	°	0	0	0	-	0	0	0	0	0
5	0.5	0.75	0.5	0.5	0.75	5.0	5.0	0.75	0.75	0.5
.:	0.85252	-	0.91140	-	0.93613	0.85252	1	0.93613	1	0.85252
6,	-	-	-	-	0.75	_	_	0.75	-	-
6,	0.85252	17710	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	17716.0	0.84665
6	0	-	0	0	0	0	0	1	1	0
3	C	-	3	2	-	4	2	1	1	4
ŭ	o	-	0	0	2	0	0	1	1	0
.;	0.5	0.75	0.5	5.0	51	0.5	6.0	0.75	67.0	0.5
٠.	0.85252	-	0.91140	-	-	0.85252	-	1	1	0.85252
V, (cV)	-101.12679	-37,10024	-102.01431	-32.76465	-78.97795	-103.92756	-32.44864	-39,48897	-39.09538	-104.73877
V, (cV)	20.69825	13.17125	21.41410	10.10870	28.90735	20.87050	10.07285	14.45367	13.45505	20.90891
T (0V)	34,31559	11.58941	34.65890	9.04312	31.73641	35.85539	8.89248	15.86820	12.74462	36.26840
V_ (eV)	-17,15779	-5.79470	-17.32945	4.52156	-15.86820	-17.92770	4.44624	-7.93410	-6.37231	-18.13420
E(so m) (eV)	0	-14.63489	0	-14.63489	-14.53414	0 .	-14,63489	-14.53414	-14,63489	0
DETIJIO (10, 10) (eV)	0	-1,13379	0	-1.13379	0	-1.85836	0.92918	. 0	-2.26758	-2.42526
Er (er m) (eV)	0	-13,50110	0	-13,50110	-14,53414	1.85836	-13.70571	-14,53414	-12.36731	2.42526
E(n, no no) (cV)	0	0	0	0	-14.53414	0	0	0	0	0
E. (n,10) (cV)	-63.27075	-31.63539	92012.69-	-31.63549	-48.73654	-63.27100	-31.63527	-31.63534	-31.63533	-63.27040
$E_{\tau}(alom - alom, mxp^2, AO)$ (aV)	-2.26759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
E, (1,11) (cV)	-65.53833	-32.20226	-64.71988	-32,76916	-48.73660	-65.12910	-32,56455	-31.63537	-31.63537	-63.69600
(10, rad(s)	49.7272	26.4826	43.6311	11,9890	68.9812	15.4704	21.5213	48,7771	28.9084	54,5632
E_{ν} (aV)	32,73133	17,43132	28.71875	7.89138	45.40465	10.18290	14.16571	32,10594	19.02803	35.91442
\vec{E}_n (eV)	-0.35806	-0.26130	0133540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0.27301	-0.38945
Er. (aV)	0.19649 [49]	0.35532 Eq. (13.458)	0.19649 [49]	0.15498	0.40929	0.20768	0.12944	0.40696	0.39427 [56]	0.11159
Ē_ (aV)	-0.25982	-0,08364	-0.23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0.07587	-0.33365
E (cV)	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Exfrant (aV)	-49,54347	-32,28590	48.82472	-32.87379	-49.17075	-65,33259	-32.74230	-31,78651	-31.71124	-66,36330
E (4 111) (aV)	-14,63489	-14.63489	-14,63489	-14.63489	-14,53414	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
E (c 11 11) (eV)	0	-13,59844	0	0	-13,59844	0	0	-13.59844	-13,59844	0
1. 1. (cV)	5.63881	3.90454	4.92005	3.60401	7.43973	6.79303	3.47253	3.51208	3.32988	7.82374

C - N - C Total Bond Evergy.
(eV)
(eV) CH (ii) Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [2].

Formula Name C = C - N (b) C = C - N (c) C = C - N (c) C = C - N (d) C = C - N (d) C = C - N (d) C = C - N (e) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C = C - N (f) C

	annual area												-						
Albana of Angle	2c.	75.	Tain.	E,	_	E. Cramman	Atons 2 Hybridization	6	5	ر- ر	ປົ	٠,٠	v	E.	ω, ;	6 - (6	Cal. 6	Exp. 6
	(°)	(°)	Years (°)		Dusignation (Table 15.3B)		Designation (Table 15.3B)	i -										 E	_
HNH7	1.\$F26x	(жұзу)	3,1559	-14.53414	z	I	T	0,93613 Eq. (13.248))	-	-	-	27.0	1,06123		-		<u> </u>	13.89	113.9 [1] (aniline)
,	1 1126X	2,69190	4,0497	-14.53414	z	-15.95955	·c	0.84665 (Eq. (15.152))	0,16214 (Eq. (15,64))	0.73		0.75	1,01912	0			_	922	21
ZH,C,N, ZH,C,N,	2.06598	234147	3,9497	-14,82575	_	-14,53414	z	17716.0	0.91140 Eq. (15.116))	0.75	-	57.0	0,99312	c				117.63	5 7
.N.Z.HZ	1,02241	2,60766	1990'1	-16,36125	01	-14.53414	Z	0.113159	0.84665 Eq. (15.152)}	0.75	-	6.75	1.01811	0				sca!	921
ZH,C,N,			L	 -								Ŀ			-	12.35	112.64	125.02	611
2H,N,C, 2H,N,C,	1.8258	2.602#7	4.0H97	-14,53414	z	-13.95955	و	0.x4665 (Eq. (13.152))	0,86284 (Eq. (15.64))	0.75	-	6.75	1.10912	0				128.35	137
ZN,C,N,	2,60766	2,60287	43359	-16.21952	=	46x60.41-	7	0,83885	0,84833	_	-	-	0,84359	-1,44915	-	-	-	112.64	1144
ZN,C,N,	254147	2,60287	4.6260	-14,53414	z	-14.53414	Z	0.91140 Eq. (15.116)	0.84665 Eq. (15.152)	-	-	-	0.\$7902	-1,44915	<u> </u>		-	133.11	127.8
ZN'C.'N"	2,54147	2,54147	45826	-(5.55033	·	-15,55033	c	0.37495	0,87495		-	·_	56743'0	-1.44915	\vdash	-	F	128.73	128.9
ZN'C."N"	2.54147	2,69190	4.5826	-13,91261	\$	-13.39265	2	0.85503	0.8392	-	-	-	0.86947	-1.44915			_	1771	119.7
מא'נ''נ"	2.70148	262936	43818	-14,53414	Z	.15.95955 C _e	¥	0.84665 (Eq. (15.152))	0.15252	-	-	; -	0.14958	-1,44915			-	110.56	110.4
"S'J'NZ	2.60287	2.62936	4.1952	-14.53414	z	-16.99103 C _s	16	0.84665 (Eq. (15.152))	0.10076	-	-	-	0.12371	-1,44915				106.60	6.201
"2'2'N"	2.54147	2.62936	144731	-14.53414	Z	.16 Politic	\$	0.91140 Eq. (15.116)	0.80076	-	-	-	0.83608	-1,44915				119.73	126.4
ZN,C,C,	2.54147	2.62936	4,4721	-14.53414	z	. 16.591ti	91	0.91340 Eq. (15.116)	0.10076	-	-	-	0.85608	-1.44915			<u> </u>	119.73	2311
מא"נ."כ"	2.69190	35629.7	4.5607	-14,53414	z	-16.52644 C.,	12	0.91140 Eq. (15.116)	0.82327	-	-	-	0.86734	-1,44915		-	-	76,711	1.221
<i>באיניני</i> "	2,70148	2.62936	4.8990	-14.53414	z	.14.82575 C.	-	0.91140 E4. (15.116)	17716.0	: 1	-	-	0.91456	-1,44915			-	35.001	132.8
7C,N,C,	2,70148	2.60766	_	-17.92022	n	17.92022	23	0,75924	0,75924	-	-	-	0.75924	-1.35836		-	 -	106,93	103.3
'.5'N'.)7	2,60287	2,60287	12661	-17.75502		-17.73502	23	0.76631	0.74631	-	-	-	0.76631	-1.85836	-	-	F	110.01	1.901
4C,N,C,	2.54147	2.54147	4,3589		. 12.	-17.75502	25	0,78155	0,76631	-	-	_	6,77393	-1,85836			F	118,09	1113
ZC, N, C,	2,54147	2.54147	4,3704	-17.71560	24	-17,40869	21	0.76801	0.78155	-	-	-	0,77478	-1.85836		_		118.59	118.6
2.7.22	2,62936	262936 2.62936	4,4731		77	-17,14871	2	0.76801	0.79340	_	-	-	0.78071	1 858 %	r	ŀ	F	114.53	1771

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While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

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